

RESEARCH ARTICLE

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 physico-chemical 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] where 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)

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[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 CaCl_2) 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 (0.1mol) was added in round bottom flask and this mixture was kept in ice bath for few minutes. Further, propanoic acid (0.11mol) 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 N_2 atmosphere.

Synthesized PIL was characterized by 1H NMR, ^{13}C NMR (Bruker Avance 400 MHz) and FTIR (JASKO FT/IR-4100) spectroscopic techniques. NMR was recorded in $CDCl_3$. 1H 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 $3400\text{--}2800\text{ cm}^{-1}$ corresponds to the characteristic ammonium peak, $\nu(N-H)$ and $\nu(O-H)$ stretching vibration. The broad band centered around 1600 cm^{-1} corresponds to the characteristic carbonyl, $\nu(C=O)$ stretching and $\delta(N-H)$ 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 ≈ 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, ρ 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) $\text{mol}\cdot\text{kg}^{-1}$ 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) $\text{kg}\cdot\text{m}^{-3}$ and speed of sound from (1000 to 2000) $\text{m}\cdot\text{s}^{-1}$. 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 $\pm 7\times 10^{-3}\text{ kg}\cdot\text{m}^{-3}$ and $\pm 0.5\text{ m}\cdot\text{s}^{-1}$, 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 $\pm 1.03\cdot 10^{-5}\text{ mol}\cdot\text{kg}^{-1}$.

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, $K_{s,2,\phi}$. In this study, the apparent molar volume, $V_{2,\phi}$ and apparent molar isentropic compression, $K_{s,2,\phi}$ of AA in water and in $m_B = (0.10, 0.15, 0.20, \text{ and } 0.25)$ $\text{mol}\cdot\text{kg}^{-1}$ aqueous solutions of [DEEA][Pro] at different temperatures (Table 1) were determined from density and speed of sound data

Table 1. The densities, ρ , apparent molar volumes, $V_{2,\phi}$, speeds of sound, u and apparent molar isentropic compression, $K_{s,2,\phi}$ 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	$^a m_B$ mol·kg ⁻¹	$^b m$ mol·kg ⁻¹	$\rho \cdot 10^{-3}$ kg·m ⁻³	$V_{2,\phi} \cdot 10^6$ m ³ ·mol ⁻¹	u m·s ⁻¹	$10^{15} \cdot K_{s,2,\phi}$ m ³ ·mol ⁻¹ ·Pa ⁻¹
293.15	0.0		($^c \rho_o = 0.998206$)		($^d u_o = 1482.84$)	
		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			($^c \rho_o = 0.997049$)		($^d u_o = 1496.85$)	
		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			($^c \rho_o = 0.995660$)		($^d u_o = 1509.25$)	
		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			($^c \rho_o = 0.994045$)		($^d u_o = 1519.82$)	
		0.06924	0.998811	107.01	1521.41	-4.01
		0.10269	1.001083	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			($^c \rho_o = 0.992228$)		($^d u_o = 1528.89$)	
		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			($^c \rho_o = 0.990223$)		($^d u_o = 1536.56$)	
		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)

<i>T/K</i>	$^a m_B$ mol·kg ⁻¹	$^b m$ mol·kg ⁻¹	$\rho \cdot 10^{-3}$ kg·m ⁻³	$V_{2,\phi} \cdot 10^6$ m ³ ·mol ⁻¹	u m·s ⁻¹	$10^{15} \cdot K_{s,2,\phi}$ m ³ ·mol ⁻¹ ·Pa ⁻¹
323.15		0.33464	1.012253 ($\rho_o = 0.9888030$)	108.32	1545.39 ($^d u_o = 1542.73$)	1.51
		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			($\rho_o = 0.985690$)		($^d u_o = 1547.61$)	
		0.06924	0.990343	109.00	1548.43	4.07
		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	0.10		($\rho_o = 0.999919$)		($^d u_o = 1499.13$)	
		0.03740	1.002499	106.86	1500.41	-3.60
		0.06114	1.004132	106.78	1501.22	-3.58
		0.12575	1.008552	106.56	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			($\rho_o = 0.998732$)		($^d u_o = 1512.18$)	
		0.03740	1.001277	107.85	1513.00	1.08
		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			($\rho_o = 0.997302$)		($^d u_o = 1523.70$)	
		0.03740	0.999822	108.58	1524.37	4.49
		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			($\rho_o = 0.995657$)		($^d u_o = 1523.36$)	
		0.03740	0.998153	109.31	1534.45	6.17
		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)

Table 1. (Continued)

<i>T/K</i>	$^a m_B$ mol·kg ⁻¹	$^b m$ mol·kg ⁻¹	$\rho \cdot 10^{-3}$ kg·m ⁻³	$V_{2,\phi} \cdot 10^6$ m ³ ·mol ⁻¹	u m·s ⁻¹	$10^{15} \cdot K_{s,2,\phi}$ m ³ ·mol ⁻¹ ·Pa ⁻¹
		0.32896	1.017589 ($^c \rho_o = 0.993814$)	107.28	1539.62 ($^d u_o = 1542.00$)	6.53
313.15		0.03740	0.996285	110.07	1542.85	10.53
		0.06114	0.997860	109.77	1543.15	10.60
		0.12575	1.002098	109.61	1543.99	10.69
		0.14367	1.003299	109.34	1544.16	10.74
		0.21169	1.007759	109.00	1544.92	10.85
		0.27537	1.011956	108.54	1545.51	10.95
		0.32896	1.015446	108.29	1546.01	11.03
318.15			($^c \rho_o = 0.991786$)		($^d u_o = 1548.91$)	
		0.03740	0.994243	110.54	1549.79	12.76
		0.06114	0.995806	110.30	1550.01	12.80
		0.12575	1.000031	110.02	1550.59	12.91
		0.14367	1.001225	109.75	1550.69	12.98
		0.21169	1.005670	109.38	1551.20	13.03
		0.27537	1.009854	108.90	1551.56	13.10
		0.32896	1.013333	108.64	1551.86	13.17
323.15			($^c \rho_o = 0.989577$)		($^d u_o = 1554.41$)	
		0.03740	0.992010	111.27	1555.14	14.41
		0.06114	0.993558	111.04	1555.31	14.41
		0.12575	0.997740	110.78	1555.76	14.47
		0.14367	0.998923	110.51	1555.83	14.51
		0.21169	1.003326	110.13	1556.19	14.58
		0.27537	1.007422	109.83	1556.49	14.64
		0.32896	1.010879	109.50	1556.67	14.70
328.15			($^c \rho_o = 0.987199$)		($^d u_o = 1558.62$)	
		0.03740	0.989618	111.77	1558.77	16.16
		0.06114	0.991153	111.61	1558.88	16.14
		0.12575	0.995303	111.37	1559.15	16.25
		0.14367	0.996478	111.10	1559.17	16.29
		0.21169	1.000851	110.71	1559.35	16.33
		0.27537	1.004965	110.23	1559.41	16.39
		0.32896	1.008382	109.98	1559.46	16.46
			($^c \rho_o = 1.000704$)		($^d u_o = 1506.73$)	
293.15	0.15	0.05512	1.004497	106.88	1508.81	-2.16
		0.07286	1.005719	106.74	1509.37	-2.14
		0.11890	1.008869	106.56	1510.83	-2.10
		0.22113	1.015818	106.15	1514.00	-2.00
		0.27993	1.019776	105.95	1515.80	-1.95
		0.40125	1.027840	105.61	1519.50	-1.87
		0.45594	1.031449	105.43	1521.12	-1.83
			($^c \rho_o = 0.999489$)		($^d u_o = 1519.38$)	
298.15		0.05512	1.003234	107.80	1521.56	1.87
		0.07286	1.004440	107.66	1522.02	1.91
		0.11890	1.007543	107.55	1523.22	2.00
		0.22113	1.014361	107.30	1525.89	2.04
		0.27993	1.018234	107.18	1527.39	2.13
		0.40125	1.026161	106.83	1530.44	2.20

(Continued)

Table 1. (Continued)

<i>T/K</i>	^a <i>m_B</i> mol·kg ⁻¹	^b <i>m</i> mol·kg ⁻¹	$\rho \cdot 10^{-3}$ kg·m ⁻³	$V_{2,\phi} \cdot 10^6$ m ³ ·mol ⁻¹	<i>u</i> m·s ⁻¹	$10^{15} \cdot K_{s,2,\phi}$ m ³ ·mol ⁻¹ ·Pa ⁻¹
		0.45594	1.029681 (^c $\rho_o = 0.998041$)	106.71	1531.79 (^d $u_o = 1530.40$)	2.26
303.15		0.05512	1.001743	108.64	1531.25	5.30
		0.07286	1.002929	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 (^c $\rho_o = 0.996383$)	107.65	1539.59 (^d $u_o = 1539.88$)	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 (^c $\rho_o = 0.994528$)	108.50	1548.87 (^d $u_o = 1544.26$)	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 (^c $\rho_o = 0.992490$)	109.14	1548.86 (^d $u_o = 1547.14$)	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 (^c $\rho_o = 0.990281$)	110.09	1551.02 (^d $u_o = 1559.57$)	13.90
323.15		0.05512	0.993841	111.59	1560.29	15.10
		0.07286	0.994987	111.47	1560.40	15.14
		0.11890	0.997932	111.38	1560.71	15.17
		0.22113	1.004384	111.24	1561.39	15.25
		0.27993	1.008079	111.03	1561.73	15.28
		0.40125	1.015571	110.76	1562.44	15.36
		0.45594	1.018910 (^c $\rho_o = 0.987911$)	110.63	1562.72 (^d $u_o = 1563.51$)	15.41
328.15		0.05512	0.991440	112.29	1563.86	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

(Continued)

Table 1. (Continued)

<i>T/K</i>	$^a m_B$ mol·kg ⁻¹	$^b m$ mol·kg ⁻¹	$\rho \cdot 10^{-3}$ kg·m ⁻³	$V_{2,\phi} \cdot 10^6$ m ³ ·mol ⁻¹	u m·s ⁻¹	$10^{15} K_{s,2,\phi}$ m ³ ·mol ⁻¹ ·Pa ⁻¹
		0.45594	1.016151	111.63	1565.14	17.61
			($\rho_o = 1.001486$)		($^d u_o = 1514.29$)	
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
			($\rho_o = 1.000251$)		($^d u_o = 1526.52$)	
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	1.033766	106.76	1539.48	2.68
			($\rho_o = 0.998785$)		($^d u_o = 1537.14$)	
303.15		0.05334	1.002327	109.39	1537.85	5.87
		0.10306	1.005613	109.18	1538.93	5.88
		0.11587	1.006469	109.03	1539.18	5.91
		0.16129	1.009459	108.84	1540.12	5.98
		0.28817	1.017700	108.49	1542.72	6.10
		0.31479	1.019446	108.31	1543.19	6.14
		0.50949	1.031941	107.54	1546.74	6.32
			($\rho_o = 0.997109$)		($^d u_o = 1546.21$)	
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
			($\rho_o = 0.995237$)		($^d u_o = 1553.79$)	
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
			($\rho_o = 0.993184$)		($^d u_o = 1559.98$)	
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)

<i>T/K</i>	^a <i>m_B</i> mol·kg ⁻¹	^b <i>m</i> mol·kg ⁻¹	$\rho \cdot 10^{-3}$ kg·m ⁻³	$V_{2,\phi} \cdot 10^6$ m ³ ·mol ⁻¹	<i>u</i> m·s ⁻¹	$10^{15} \cdot K_{s,2,\phi}$ m ³ ·mol ⁻¹ ·Pa ⁻¹
323.15		0.50949	1.025399 ($\rho_o = 0.990963$)	109.68	1563.29 ($u_o = 1564.84$)	14.22
		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
		0.50949	1.022542	111.08	1568.14	15.84
328.15			($\rho_o = 0.988575$)		($u_o = 1568.48$)	
		0.05334	0.991952	113.00	1569.01	17.90
		0.10306	0.995078	112.86	1569.18	17.88
		0.11587	0.995879	112.83	1569.21	17.94
		0.16129	0.998707	112.73	1569.35	17.97
		0.28817	1.006483	112.54	1569.72	18.09
		0.31479	1.008114	112.43	1569.76	18.12
		0.50949	1.019731	112.06	1570.18	18.28
293.15	0.25		($\rho_o = 1.002344$)		($u_o = 1522.61$)	
		0.05459	1.006053	107.69	1524.90	-0.37
		0.08555	1.008156	107.47	1525.83	-0.28
		0.12314	1.010692	107.35	1526.97	-0.25
		0.14154	1.011952	107.13	1527.48	-0.20
		0.19493	1.015563	106.81	1529.00	-0.10
		0.23030	1.017941	106.65	1530.00	-0.05
		0.24087	1.018665	106.54	1530.27	-0.02
298.15			($\rho_o = 1.001089$)		($u_o = 1534.27$)	
		0.05459	1.004751	108.60	1536.29	3.56
		0.08555	1.006821	108.46	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	107.95	1539.67	3.77
		0.23030	1.016441	107.77	1540.47	3.83
		0.24087	1.017159	107.64	1540.68	3.85
303.15			($\rho_o = 0.999601$)		($u_o = 1544.44$)	
		0.05459	1.003222	109.42	1546.25	7.34
		0.08555	1.005269	109.27	1546.84	7.37
		0.12314	1.007744	109.13	1547.54	7.43
		0.14154	1.008962	108.99	1547.86	7.47
		0.19493	1.012472	108.72	1548.79	7.55
		0.23030	1.014796	108.52	1549.37	7.61
		0.24087	1.015513	108.36	1549.50	7.64
308.15			($\rho_o = 0.997905$)		($u_o = 1553.07$)	
		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)

Table 1. (Continued)

T/K	${}^a m_B$ $\text{mol}\cdot\text{kg}^{-1}$	${}^b m$ $\text{mol}\cdot\text{kg}^{-1}$	$\rho\cdot 10^{-3}$ $\text{kg}\cdot\text{m}^{-3}$	$V_{2,\phi}\cdot 10^6$ $\text{m}^3\cdot\text{mol}^{-1}$	u $\text{m}\cdot\text{s}^{-1}$	$10^{15}\cdot K_{s,2,\phi}$ $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1}$
		0.24087	1.013651 (${}^c \rho_o = 0.996018$)	109.13	1557.46 (${}^d u_o = 1560.26$)	9.87
313.15		0.05459	0.999566	110.93	1561.55	13.81
		0.08555	1.001572	110.78	1561.81	13.87
		0.12314	1.004002	110.59	1562.10	13.96
		0.14154	1.005195	110.46	1562.23	13.99
		0.19493	1.008649	110.12	1562.57	14.08
		0.23030	1.010925	109.94	1562.79	14.11
		0.24087	1.011611 (${}^c \rho_o = 0.993950$)	109.86	1562.84 (${}^d u_o = 1566.07$)	14.13
318.15		0.05459	0.997456	111.79	1566.87	15.38
		0.08555	0.999442	111.61	1567.05	15.51
		0.12314	1.001839	111.47	1567.27	15.58
		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	1.009296 (${}^c \rho_o = 0.991716$)	111.00	1567.84 (${}^d u_o = 1570.28$)	15.78
		0.05459	0.995197	112.37	1570.39	17.18
		0.08555	0.997174	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	1.007051 (${}^c \rho_o = 0.989322$)	111.15	1570.74 (${}^d u_o = 1573.88$)	17.42
		0.05459	0.992777	112.98	1574.02	19.32
		0.08555	0.994736	112.75	1574.01	19.37
		0.12314	0.997104	112.58	1573.98	19.46
		0.14154	0.998280	112.35	1573.92	19.53
		0.19493	1.001631	112.12	1573.83	19.61
		0.23030	1.003862	111.88	1573.71	19.69
		0.24087	1.004547	111.73	1573.64	19.71

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

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(Table 1) by using the following Eqs (1) and (2):

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

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

where M and m are respectively, the molar mass and molality of AA; ρ and ρ_o are the densities of solution and solvent (water or water + [DEEA][Pro]), κ_s and κ_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, κ_s as: $\kappa_s = u^{-2} \cdot \rho^{-1}$. 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 (0.20 to 0.04) $\cdot 10^6 \text{ m}^3 \cdot \text{mol}^{-1}$ 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 (0.60 to 0.12) $\cdot 10^{-15} \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$ 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

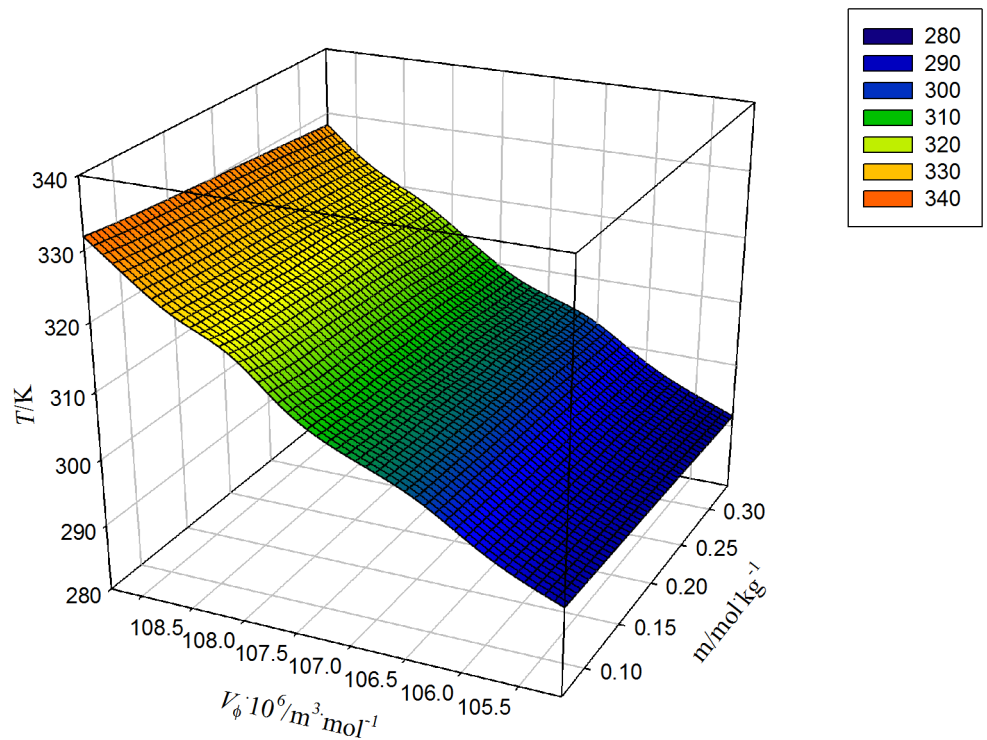


Fig 1. Plot of apparent molar volumes, V_{ϕ} versus molalities, m of ascorbic acid in water at temperatures, $T = (293.15, 298.15, 303.15, 308.15, 313.15, 318.15, 323.15 \text{ and } 328.15) \text{ K}$.

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intermediate (small and negative). Negative $K_{s,2,\phi}$ 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, $K_{s,2,\phi}$ 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 $K_{s,2,\phi}$ 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 ($V_2^\circ = V_{2,\phi}^\circ$) and partial molar isentropic compression ($K_{s,2}^\circ = K_{s,2,\phi}^\circ$) has been evaluated by least-square fitting to the corresponding data as Eqs (3) and (4):

$$V_{2,\phi} = V_2^\circ + S_V m \tag{3}$$

$$K_{s,2,\phi} = K_{s,2}^\circ + S_K m \tag{4}$$

where S_V and S_K are respective experimental slopes. Apparent molar volume, $V_{2,\phi}$ of AA in water has been reported by various workers [33, 49–52] and in few reports, $V_{2,\phi}$ 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] without considering the dissociation of AA. Dhondge et al. [40] have reported that at low concentration the effect of hydrolysis of AA on volumetric properties are assumed to be negligible (as it lies in the range of uncertainties), whereas at high concentration it is smaller due to decrease in the degree of hydrolysis. In this work, $V_{2,\phi}$ values of AA were determined by assuming that the effect of hydrolysis of AA on apparent molar volume is very small and negligible [40]. The V_2° and $K_{s,2}^\circ$ values of AA in water agree well the literature values [32, 29, 33, 49–50, 52] and are given in Tables 2 and 3, respectively. The V_2° values of AA increase with concentration of [DEEA][Pro] and temperature, which indicate an increase in interactions between ions of [DEEA][Pro] ($-\text{NH}_3^+$, $\text{C}_2\text{H}_5\text{COO}^-$) and AA, which may be due to the dominance of hydrophilic-ionic interactions. Both negative and positive $K_{s,2}^\circ$ 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, ($\Delta_t V_2^\circ$ and $\Delta_t K_{s,2}^\circ$), which is considered to be free from solute-solute interactions, and were calculated using Eq (5):

$$\Delta_t X_2^\circ = X_2^\circ \text{ (in aqueous [DEEA][Pro] solutions)} - X_2^\circ \text{ (in water)} \tag{5}$$

where $\Delta_t X_2^\circ = (\Delta_t V_2^\circ \text{ or } \Delta_t K_{s,2}^\circ)$, $X_2^\circ = (V_2^\circ \text{ or } K_{s,2}^\circ)$, the plot of $\Delta_t V_2^\circ$ versus m_B has been illustrated in Fig 2a and $\Delta_t K_{s,2}^\circ$ versus m_B in Fig 2b. The transfer parameters ($\Delta_t V_2^\circ$ and $\Delta_t K_{s,2}^\circ$) are positive and increase with concentration of newly synthesized PIL (synthesis is shown in Fig 3) and temperature. The $\Delta_t V_2^\circ$ values increase with cosolute (PIL) concentration, however a slight decrease in $\Delta_t V_2^\circ$ values from $m_B \approx (0.10 \text{ to } 0.15) \text{ mol}\cdot\text{kg}^{-1}$ have been observed, whereas $\Delta_t K_{s,2}^\circ$ values increase continuously with PIL concentration at all temperature. This behaviour in $\Delta_t V_2^\circ$ values for AA is different (only between $[0.10 \text{ to } 0.15] \text{ mol}\cdot\text{kg}^{-1}$) as compared to $\Delta_t K_{s,2}^\circ$ 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 $T = (293.15 \text{ to } 328.15) \text{ K}$.

$^a m_B / \text{mol} \cdot \text{kg}^{-1}$ $T/K =$	$V_2^\circ \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$							
	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15
0.00	105.07 $\pm 0.01^b$ (0.85) ^c	105.76 ± 0.01 (0.81)	106.25 ± 0.01 (0.83)	106.94 ± 0.01 (1.21)	107.51 ± 0.01 (0.99)	107.86 ± 0.01 (1.36)	108.44 ± 0.01 (1.40)	108.93 ± 0.01 (1.13)
		[105.95 ^d , 103.46 ^e , 106.49 ^f , 105.17 ^g , 105.40 ^{h,i} , 105.38 ^j]		[106.98 ^d , 104.98 ^e , 107.08 ^f , 106.97 ^g]		[107.94 ^d]		
0.10	107.03 ± 0.03 (-3.95)	108.05 ± 0.04 (-4.03)	108.76 ± 0.04 (-4.93)	109.50 ± 0.07 (-6.87)	110.25 ± 0.08 (-6.01)	110.75 ± 0.06 (-6.50)	111.45 ± 0.06 (-5.97)	112.03 ± 0.07 (-6.31)
0.15	107.00 ± 0.06 (-3.53)	107.89 ± 0.04 (-2.60)	108.72 ± 0.06 (-2.46)	109.53 ± 0.04 (-2.31)	110.30 ± 0.04 (-2.61)	110.02 ± 0.05 (-1.98)	111.68 ± 0.04 (-2.28)	112.33 ± 0.03 (-2.54)
0.20	107.90 ± 0.08 (-4.66)	108.71 ± 0.05 (-3.81)	109.55 ± 0.06 (-3.92)	110.33 ± 0.06 (-4.66)	111.07 ± 0.09 (-5.81)	111.77 ± 0.08 (-4.19)	112.46 ± 0.04 (-2.74)	113.08 ± 0.03 (-1.99)
0.25	108.02 ± 0.04 (-6.09)	108.90 ± 0.04 (-5.01)	109.75 ± 0.05 (-5.48)	110.52 ± 0.03 (-5.74)	111.27 ± 0.02 (-5.83)	111.98 ± 0.02 (-4.01)	112.66 ± 0.03 (-6.29)	113.32 ± 0.05 (-6.39)

^a m_B , molality of [DEEA][Pro] in water.

^bstandard deviation.

^c $S_v / \text{m}^3 \cdot \text{kg} \cdot \text{mol}^{-2}$.

^dRef [32].

^eRef [33].

^fRef [49].

^gRef [50].

^hRef [52].

ⁱRef [29].

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

$^a m_B / \text{mol} \cdot \text{kg}^{-1}$ $T/K =$	$K_{s,2}^\circ \cdot 10^{-15} / \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$							
	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15
0.00	-12.25 $\pm 0.01^b$ (1.23) ^c	-8.68 ± 0.02 (1.38)	-5.60 ± 0.02 (1.19)	-4.08 ± 0.01 (1.21)	-0.08 ± 0.01 (1.11)	1.03 ± 0.02 (1.38)	2.48 ± 0.01 (1.26)	3.97 ± 0.02 (1.22)
		[-8.04 ^d , -7.10 ^e , -9.00 ^f]		[-4.06 ^d , -4.00 ^e]		[0.99 ^d]		
0.10	-3.64 ± 0.02 (1.27)	1.04 ± 0.01 (1.18)	4.50 ± 0.04 (1.16)	6.14 ± 0.01 (1.21)	10.48 ± 0.01 (1.69)	12.73 ± 0.03 (1.38)	14.36 ± 0.01 (1.04)	16.11 ± 0.02 (1.06)
0.15	-2.20 ± 0.01 (0.83)	1.85 ± 0.03 (0.91)	5.27 ± 0.01 (0.80)	7.07 ± 0.02 (0.78)	11.38 ± 0.01 (0.81)	13.48 ± 0.01 (0.93)	15.08 ± 0.01 (0.72)	17.25 ± 0.02 (0.80)
0.20	-1.81 ± 0.01 (1.08)	2.18 ± 0.02 (1.01)	5.80 ± 0.02 (1.04)	7.68 ± 0.01 (0.97)	11.87 ± 0.01 (1.14)	13.70 ± 0.03 (1.04)	15.38 ± 0.01 (0.91)	17.83 ± 0.02 (0.90)
0.25	-0.46 ± 0.01 (1.80)	3.48 ± 0.01 (1.54)	7.24 ± 0.01 (1.62)	9.37 ± 0.02 (1.98)	13.73 ± 0.02 (1.69)	15.32 ± 0.03 (1.94)	17.10 ± 0.01 (1.37)	19.20 ± 0.01 (2.12)

^a m_B , molality of [DEEA][Pro] in water.

^bstandard deviation.

^c $S_v / \text{m}^3 \cdot \text{kg} \cdot \text{mol}^{-2} \cdot \text{Pa}^{-1}$.

^dRef [32].

^eRef [52].

^fRef [29].

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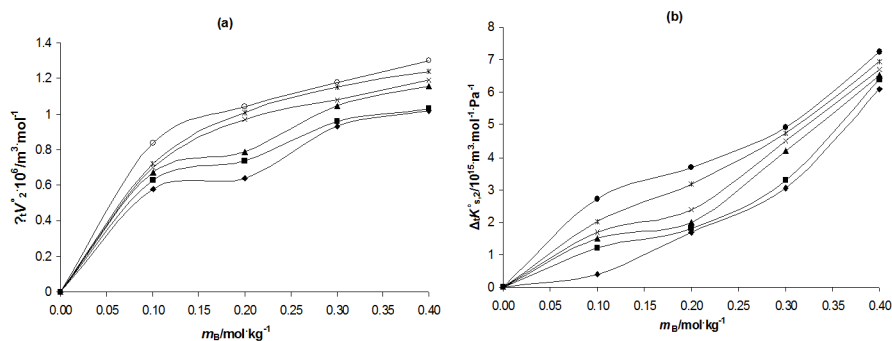


Fig 2. Plots of volumes of transfer ($\Delta_t V_2^\circ$ and $\Delta_t K_{s,2}^\circ$) versus molalities, m_B of [DEEA][Pro] of ascorbic acid. a) $\Delta_t V_2^\circ$ versus m_B ; b) $\Delta_t K_{s,2}^\circ$ versus m_B at temperatures, $T = \blacklozenge$, 293.15 K; \blacksquare , 298.15 K; \blacktriangle , 303.15 K; \times , 308.15 K; $*$, 313.15 K; \otimes , 318.15 K; $+$, 323.15 K; $-$, 328.15 K.

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Ascorbic acid has a five membered ring containing two carbonyl groups and exists as [53] 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_α and H_β (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_α or H_β). 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_β is more (shown in I of Fig 4) as compared to conjugate base generated on removal of H_α (shown in II of Fig 4). The carboxylate anion of [DEEA][Pro] will probably interact more strongly with H_β (most acidic hydrogen), which may be responsible for positive transfer volumes ($\Delta_t V_2^\circ$ or $\Delta_t K_{s,2}^\circ$), 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 $\Delta_t V_2^\circ$ values for AA, and suggested that the irregular trend in $\Delta_t V_2^\circ$ 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 $\Delta_t V_2^\circ$ and $\Delta_t K_{s,2}^\circ$ values suggest that with increase in PIL concentration and temperature, the hydrophilic-ionic types of interactions become more favorable.

The $\Delta_t V_2^\circ$ and $\Delta_t K_{s,2}^\circ$ 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 $-\text{NH}_3^+$ of PIL; b) Hydrophilic—cation interactions between ($-\text{OH}$, $-\text{C}=\text{O}$, and $-\text{O}^-$) groups of AA and $-\text{NH}_3^+$; c) Hydrophobic—anion interactions between hydrophobic parts of AA and $\text{C}_2\text{H}_5\text{COO}^-$; d) Hydrophilic—hydrophobic interactions between the hydrophilic groups of AA and hydrophobic parts of [DEEA][Pro]. According to the structural interaction model [54], type (a, c and d) interactions are repulsive as the groups involved are incompatible or inability of the groups to orient water,

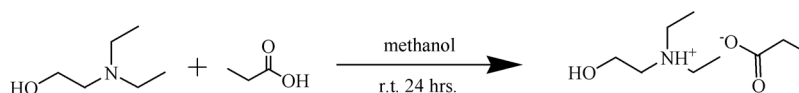


Fig 3. Synthesis of diethylethanolammonium propanoate [DEEA][Pro].

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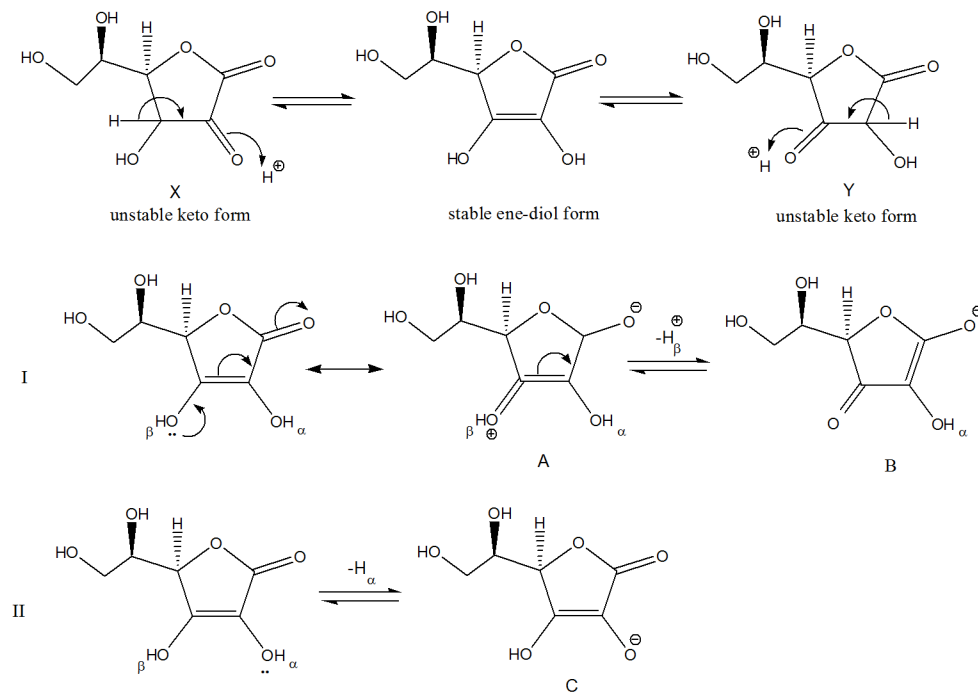


Fig 4. 1,2 Diketone (X) and 1,3-diketone (Y) form of ascorbic acid and their interconversion.

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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 ($-\text{OH}$, $-\text{C}=\text{O}$, and $-\text{O}^-$) of AA, which leads to a decrease in structure-breaking tendency of ion and thus reduction of electrostriction. Transfer volumes ($\Delta_t V_2^\circ$ and $\Delta_t K^\circ_{s,2}$) increase with cosolute concentration and temperature, which indicate dominance of hydrophilic-ionic interactions (type b) over hydrophobic type of interactions. The positive $\Delta_t V_2^\circ$ 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 $(\partial V_2^\circ / \partial T)_p$ and its second derivatives $(\partial^2 V_2^\circ / \partial T^2)_p$ have been calculated by using the following Eq (6):

$$V_2^\circ = v_o + v_1 T + v_2 T^2 \quad (6)$$

where v_o , v_1 and v_2 are constants. The derivative of V_2° with respect to temperature at constant pressure i.e. $(\partial V_2^\circ / \partial T)_p$ 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: $(\frac{\delta C_{p,2}^\circ}{\delta p})_T = -T \left(\frac{\partial^2 V_2^\circ}{\partial T^2} \right)_p$, negative $(\partial^2 V_2^\circ / \partial T^2)_p$ 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 ($\Delta_t V_2^\circ$ or $\Delta_t K^\circ_{s,2}$) based on McMillan-Mayer

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

$m_B / \text{mol} \cdot \text{kg}^{-1}$	$(\partial V_2^\infty/\partial T)_P \cdot 10^6$								SD*	$(\partial^2 V_2^\infty/\partial T^2)_P \cdot 10^6$
	$\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$									
	T/K									
	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15		
0.00	0.129	0.123	0.118	0.112	0.106	0.101	0.095	0.089	0.07	-0.001
0.10	0.176	0.166	0.155	0.145	0.135	0.124	0.114	0.104	0.08	-0.002
0.15	0.181	0.173	0.165	0.156	0.148	0.140	0.131	0.123	0.01	-0.002
0.20	0.173	0.166	0.159	0.152	0.145	0.138	0.131	0.124	0.01	-0.001
0.25	0.177	0.170	0.162	0.155	0.147	0.139	0.132	0.124	0.02	-0.002

*SD—standard deviation.

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theory [57] of solutions by using Eq (7):

$$\Delta_t Y_2^o = 2Y_{AB}m_B + 3Y_{ABB}m_B^2 \tag{7}$$

where A denotes AA and B denotes PIL ([DEEA][Pro]). Constants $Y_{AB}(V_{AB} \text{ or } K_{AB})$ and $Y_{ABB}(V_{ABB} \text{ or } K_{ABB})$ 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 [DEEA][Pro] 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 ($\Delta_t V_2^o$ and $\Delta_t K_{s,2}^o$) 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 $\Delta_t V_2^o$ and $\Delta_t K_{s,2}^o$ values suggest the dominance of hydrophilic-ionic type of interactions between the ions

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

$V_{AB} \cdot 10^6$ $\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kg}$	$V_{ABB} \cdot 10^6$ $\text{m}^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2$	$V_{AB} \cdot 10^6$ $\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kg}$	$V_{ABB} \cdot 10^6$ $\text{m}^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2$
T = 293.15 K		T = 298.15 K	
10.18	-11.42	11.84	-15.16
T = 303.15 K		T = 308.15 K	
13.37	-17.32	13.89	-18.25
T = 313.15 K		T = 318.15 K	
15.04	-20.42	16.39	-22.04
T = 323.15 K		T = 328.15 K	
17.02	-23.22	17.65	-24.01

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Table 6. The pair, K_{AB} and triplet, K_{ABB} compressibility interaction coefficients for ascorbic acid in aqueous[DEEA][Pro] solutions at temperatures, $T = (293.15$ to $328.15)$ K.

K_{AB} $m^3 \cdot mol^{-2} \cdot Pa^{-1} \cdot kg$	T	K_{ABB} $m^3 \cdot mol^{-3} \cdot Pa^{-1} \cdot kg^2$	T	K_{AB} $m^3 \cdot mol^{-2} \cdot Pa^{-1} \cdot kg$	K_{ABB} $m^3 \cdot mol^{-3} \cdot Pa^{-1} \cdot kg^2$
50.86	$T = 293.15$ K	-75.33	$T = 298.15$ K	56.52	-89.24
58.07	$T = 303.15$ K	-89.86	$T = 308.15$ K	58.33	-87.39
60.05	$T = 313.15$ K	-90.42	$T = 318.15$ K	67.68	-108.69
68.33	$T = 323.15$ K	-108.75	$T = 328.15$ K	71.29	-112.65

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of PIL and hydrophilic sites 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. $(\partial^2 V_2^\circ / \partial T^2)_P$ 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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