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Volumetric properties of Vitamin C in aqueous LiCl solution at T= (288.15 to 318.15) K

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Abstract

Vit. C (L-ascorbic acid) is an essential vitamin required by the living system. Densities (*d*) of Vit. C in water and in aqueous solution of LiCl has been determined at temperature T=(288.15-318.15) K at atmospheric temperature. The values of densities increase with increases in concentrations and decreases with temperature. The apparent molar volume **(V_ϕ)** and partial molar volume (V_2^o) have been calculated from the density data for the studied aqueous solutions of Vit. C in water and in aqueous LiCl solutions. The partial transfer volume of **($\Delta_{tr}V_2^o$)** for Vit. C form water to aqueous solution have been calculated. The Values of $(\partial V_2^o/\partial T)_p$ and $(\partial^2 V_2^o/\partial T^2)_p$ have been deduced from data to predict the structure making and breaking nature of Vit.C in water and in aqueous solutions of LiCl at all the studied temperatures.

Introduction

Vitamins are organic nutrients components necessary in small quantities to catalyze biochemical reactions, can only be supplied from external sources in the diet. [1] Vitamins can be classified into two types depending upon the medium in which they are soluble; (1) Fat soluble (2) Water soluble.

The biological function of Vit.C appear to exhibit reducing properties and easy one-electron reduction to dehydroascorbic acid. [2] This acid is in equilibrium with hydrated hemiacetal. iThe weak acid Vit.C also express metal complexing properties.

An electrolyte' on dissolution in water disturb the arrangement of water molecules due to presence of electric field of its ions. [3, 4]**.** Various biological process, where water is present as main solvent, metallic ions play verity of vital roles. The biofluids are associated with almost constant composition of certain electrolytes, the most important of which being

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sodium chloride [5] It is necessary to study the interactions of vitamin in aqueous electrolyte solution to understand the mechanism of action in detail. To study the molecules interactions in solution, the thermodynamic and transport method like partial molar volume, viscosity compressibility are the best approaches. The partial molar volume which is a first derivative of Gibbs free energy is very helpful for interpreting solute-solvent interactions. Apelblat and Manzurola [6] determined the apparent molar volumes of ascorbic acid in water 298.15 K had not taken into consideration the ionization of the organic acid, which could be a determenentle factor particularly at low concentration.

Kaulgud et.al.[7] reported the thermodynamic (density and compressibility) and Transport (Viscosity) properties of ascorbic acid dilute aqueous solutions and aqueous solution of electrolytes (0.06m NaCl). The Results have been reported in terms of solute-solvent interactions at very low concentration of electrolyte.

Hakin et.al [8] reported the volumetric and thermochemical properties of L-ascorbic acid in water at three temperatures Ayranci et.al[5] measured the density and sound velocity data in water and aqueous NaCl solutions at T=(283.15-313.15) K and reported the thermodynamic parameters of Vit. C (L-ascorbic acid). The positive and negative values of $\Delta_{tr}V_2^o$ indicate the complex interaction between the studied vitamins (L-Ascorbic Acid and Pyridoxine HCl) with NaCl. From the above review of literature, it is clear the no report on interactions of Vit. C (L-ascorbic acid) with lithium chloride is available. So based upon these in present research article partial molar volumes of Vit. C (ascorbic acid) in water and in aqueous lithium chloride solution (0.1, 0.25, 0.5, 1.0) (m_B = molality of LiCl in $mol \cdot kg^{-1}$) have been determined at T=(288.15-318.15) K from density measurements using vibrating tube digital density meter. further from the data collected partial molar volumes of transfer expansibilities and second derivatives of partial molar volumes have deduced to know the structure making or breaking ability of the solute (Vit.C) in the presence of consulate (LiCl) in aqueous media at studied temperature.

Experimental

Chemicals used in the present work are listed in the Table 1, along with their sources and grades.

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Table 1 : Sources and Grades of Chemicals Used

S.No.	Compound	Source	Grade
1.	Vit. C (L-Ascorbic Acid)	SRL	AR
2.	Lithium Chloride	SRL	AR

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NO further p purification of chemicals was done before doing the experiments. However, before use, all he chemicals were dried in the oven for 24 hours and then placed in a vacuum desiccator having $CaCl_2$.

Conductivity water was prepared by doubly distilling the deionized water. It was first distilled using acidified $KMnO_4$ followed by the alkaline $KMnO_4$ in a double stage glass distillation apparatus. Mettler Balance with an accuracy of ± 0.01 mg is used for weighing. Digital densimeter Anton Paar DMA 60/602have been used to measure the densities. The accuracy, precision and calibration of densimeter have been discussed elsewhere [9].

Results and Discussion

The apparent molar volumes, V_ϕ of Vit. C in water and in aqueous solutions of lithium chloride at temperature 288.15, 298.15, 308.15 and 318.15 K calculated from densities, d and are given in Table 2. The relation used to calculate V_ϕ is given below:

$$V_\phi = (M/d) - [(d - d_o)1000] / (m d d_o) \quad \ldots 1$$

Here M and m are the molar mass and molality of the ascorbic acid and d and d_o the densities of solution and solvent respectively, . The linear equation given below can be used to obtain partial molar volume (V_2^o) from V_ϕ.

$$V_\phi = V_2^o + S_v m \quad \ldots 2$$

In equation 2, S_v is the experimental slope. The V_2^o values for the ascorbic acid have increased with increase in temperature in LiCl. When we plot a graph between V_ϕ and m of ascorbic acid, a straight line have been obtained and in LiCl solutions at all temperature in question . Hence we given only one graph in Fig. (1).

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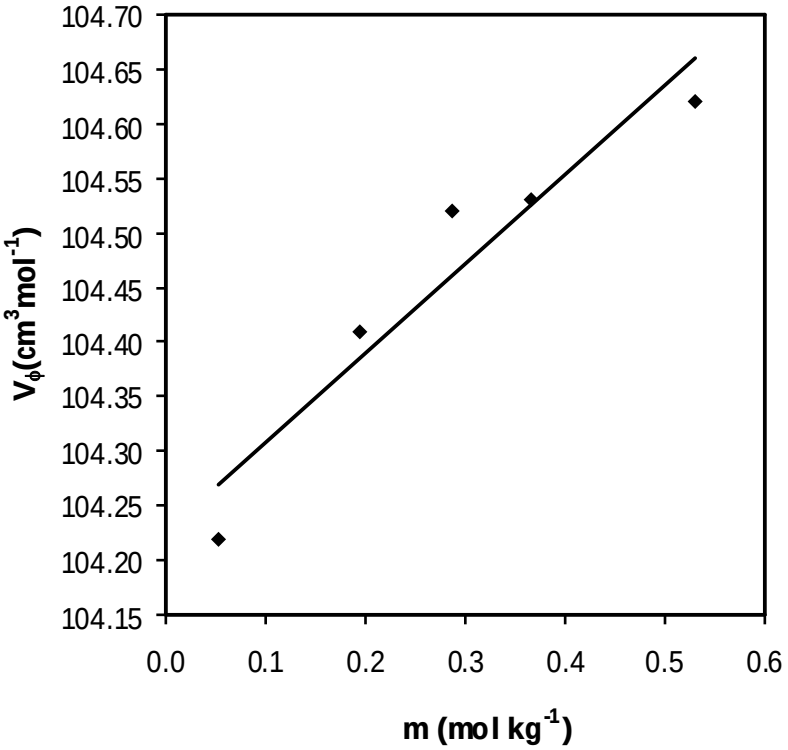

Fig.1: Vit. C in water at 298.15 K

Table 2 : Molality; m, Densities; *d*, apparent molal volumes; V_ϕ of Vit. C in water and in aqueous LiCl solutions at at T=(288.15-318.15) K.

m mol·kg^{-1}	*d* g·cm^{-3}	V_ϕ cm^3·mol^{-1}		m mol·kg^{-1}	*d* g·cm^{-3}	V_ϕ cm^3·mol^{-1}
Vit. C in water						
288.15 K						
0.05239	1.002876	104.22		0.28757	1.019128	104.52
0.13686	1.008847	104.13		0.36561	1.024354	104.53
0.19345	1.012733	104.41		0.53046	1.035084	104.62
298.15 K						
0.05239	1.00715	105.82		0.28757	1.016645	106.01
0.13686	1.006573	105.62		0.36561	1.021743	106.08
0.19345	1.010376	105.93		0.53046	1.032264	106.12
308.15 K						

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0.05239	0.99768	106.93	0.2857	1.013421	106.98
0.13686	1.003439	106.84	0.36561	1.018437	107.09
0.19345	1.007231	106.88	0.53046	1.028804	107.16
318.15 K					
0.05239	0.993801	108.23	0.28757	1.009341	108.06
0.13686	0.999514	107.78	0.36561	1.014315	108.10
0.19345	1.003233	107.98	0.53046	1.024546	108.17
At m_B = 0.1 mol·kg^{-1}					
288.15 K (d_o = 1.001153)					
0.06277	1.006165	104.23	0.25253	1.019353	104.27
0.10983	1.009477	104.32	0.31076	1.023253	104.41
0.12831	1.010798	104.10	0.35235	1.025998	104.53
0.20286	1.015923	104.40	0.42507	1.030738	104.68
298.15 K (d_o = 0.998992)					
0.06277	1.003951	106.07	0.25253	1.016925	105.64
0.10983	1.007280	105.25	0.31076	1.020744	105.81
0.12831	1.008528	105.48	0.35235	1.023395	106.04
0.20286	1.013627	105.43	0.42507	1.028071	106.10
308.15 K (d_o = 0.996038)					
0.06277	1.000887	107.11	0.25253	1.013628	106.92
0.10983	1.004122	106.75	0.31076	1.017410	106.99
0.12831	1.005369	106.79	0.35235	1.020040	107.16
0.20286	1.010335	106.97	0.42507	1.024670	107.17
318.15 K (d_o = 0.992213)					
0.06277	0.997039	107.51	0.25253	1.009638	107.71
0.10983	1.000244	107.32	0.31076	1.013365	107.85
0.12831	1.001466	107.50	0.35235	1.015953	108.05
0.20286	1.006379	107.74	0.42507	1.020521	108.09
At m_B == 0.25 mol·kg^{-1}					
288.15 K (d_o = 1.004487)					
0.05247	1.008742	104.41	0.23237	1.021150	104.79

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0.10664	1.12549	104.46	0.29025	1.025039	104.84
0.13566	1.014549	104.63	0.33494	1.028005	104.88
0.16449	1.016545	104.61	0.41427	1.033200	104.93
298.15 K (d_o = 1.002296)					
0.05247	1.006553	105.45	0.23237	1.018739	106.05
0.10664	1.010283	105.73	0.29025	1.022582	106.02
0.13566	1.012263	105.79	0.33494	1.025456	106.19
0.16449	1.014165	106.16	0.41427	1.030541	106.28
308.15 K (d_o = 0.999304)					
0.05247	1.003458	107.04	0.23237	1.015474	107.21
0.10664	1.00713	107.10	0.29025	1.019236	107.25
0.13566	1.009075	107.14	0.33494	1.022103	107.29
0.16449	1.0110012	107.14	0.41427	1.027116	107.37
318.15 K (d_o = 0.995498)					
0.05247	0.999598	108.01	0.23237	1.01147	108.20
0.10664	1.003226	108.08	0.29025	1.015192	108.22
0.13566	1.005157	108.07	0.33494	1.018023	108.27
0.16449	1.007048	108.15	0.41427	1.022976	108.35
At m_B = 0.5 mol·kg^{-1}					
288.15 K (d_o = 1.009713)					
0.05383	1.014329	105.07	0.24511	1.027537	104.65
0.09294	1.017104	104.50	0.29863	1.031069	104.86
0.16843	1.022327	104.57	0.36945	1.035722	104.95
0.18443	1.023424	104.58	0.42245	1.039144	105.03
298.15 K (d_o = 1.007536)					
0.05383	1.012037	106.92	0.24511	1.025008	106.08
0.09294	1.014717	106.62	0.29863	1.028476	106.27
0.16843	1019898	106.03	0.36945	1.033012	106.42
0.18443	1.020877	106.54	0.42245	1.036371	106.48
308.15 K (d_o = 1.004514)					
0.05383	1.008999	107.18	0.24511	1.021765	107.06

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0.09294	1.01164	107.24	0.29863	1.025153	107.37
0.16843	1.016677	107.27	0.36945	1.029661	107.41
0.18443	1.017738	107.25	0.42245	1.032984	107.45
318.15 K (d_o = 0.995498)					
0.05247	0.999598	108.01	0.23237	1.017775	108.00
0.09294	1.007799	107.83	0.29863	1.02114	108.24
0.16843	1.012758	108.13	0.36945	1.025603	108.27
0.18443	1.013798	108.16	0.42245	1.028895	108.30
At m_B = 1.0 mol·kg^{-1}					
288.15 K (d_o = 1.020280)					
0.04842	1.025014	104.90	0.26249	1.03948	105.37
0.10143	1.02868	104.98	0.29590	1.041692	105.34
0.14770	1.031828	105.14	0.33917	1.044491	105.43
0.22225	1.036831	105.26	0.38350	1.047332	105.51
298.15 K (d_o = 1.017937)					
0.04842	1.022665	105.76	0.26249	1.036883	106.52
0.10143	1.026274	105.98	0.29590	1.03906	106.49
0.14770	1.029362	106.25	0.33917	1.041819	106.57
0.22225	1.034282	106.39	0.38350	1.044578	106.73
308.15 K (d_o = 1.014863)					
0.04842	1.01957	106.58	0.26249	1.033577	107.57
0.10143	1.023128	106.93	0.29590	1.035723	107.53
0.14770	1.026176	107.20	0.33917	1.038454	107.57
0.22225	1.031032	107.35	0.38350	1.041133	107.85
318.15 K (d_o = 1.011153)					
0.04842	1.015763	107.68	0.26249	1.029615	108.48
0.10143	1.019242	108.30	0.29590	1.031705	108.55
0.14770	1.022255	108.42	0.33917	1.034382	108.64
0.22225	1.027067	108.42	0.38350	1.037098	108.72

m_B=molality of LiCl solutions.

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The partial molar volume of transfer $\Delta_{tr}V_2^o$ for the studied ascorbic acid from water to aqueous lithium chloride solutions as follow.

$\Delta_{tr}V_2^o = V_2^o$ (in aqueous solution of consulate) – V_2^o (in water) …3

value of The observed $\Delta_{tr}V_2^o$ are positive and negative (Table 3) for ascorbic acid in aqueous solution of lithium chloride. The $\Delta_{tr}V_2^o$ value does not follow any regular trend in the studied consulates i.e. LiCl. This may be due to complex interaction between (organic acid like) Vit. C and aqueous solution of lithium chloride.

Table 3: Partial molar volumes of transfer of Vit. C from water to aqueous solutions of LiCl.

m_B. mol·kg^{-1}	$\Delta_{tr}V_2^o$			
	288.15K	**298.15K**	**308.15K**	**318.15K**
0.10	-0.06	-0.90	-0.13	-0.73
0.25	0.13	-0.35	0.27	0.08
0.50	0.06	-0.13	0.42	0.14
1.00	0.60	-0.07	-0.16	0.27

The least-square into equation can be applied to the collected data for having an idea of effect of temperature on volumetric properties

$$V^2 = a + bT + cT^2 \quad \ldots 4$$

In this equation a, b and c are constant, T is the temperature. Partial molar expansibilities $(\partial V_2^o/\partial T)_p$ and second derivative $(\partial^2 V_2^o/\partial T^2)_P$ values calculated from the above equation are given in Table 4.

The V_E^o values of Vit. C decrease regularly in water when temperature changes from 288.15 – 318.15 K. Further these value decrease in continuous manner for (0.1, 0.25, 0.5) m_B of lithium chloride for the studied temperature. But in the presence of 1.0 m_B lithium chloride the expansibilities value increase with temperature.

The qualitative data from Hepler's method [10] to predict the hydration of solutes in aqueous system, during thermal expansion can be obtained using following relation

$$(\partial Cp^o{}_2/\partial_P)_T = -T(\partial^2 V_2^o/\partial T^2)_P \quad \ldots 5$$

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According to this relation left-side equation is positive for a structure breaking solutes and therefore structure breaking solutes should have negative $(\partial^2 V_2^o/\partial T^2)_P$ while structure making solute should have positive value.

Presently the values of $(\partial^2 V_2^o/\partial T^2)_P$ are positive for water which suggest that Vit. C behave as a structure maker in water (Table 4). In aqueous Lithium chloride the values of $(\partial^2 V_2^o/\partial T^2)$ are negative at (0.1, 0.25,0.5) m_B which means Vit. C behaves as structure breaker at these concentrations (Table 4). However, the positive value at 1.0 m_B suggest that Vit. C behaves as structure maker.

Tables 4: $(\partial V_2^o/\partial T)_P$ and $(\partial^2 V_2^o/\partial T^2)_P$ values of Vit. C at concentration of LiCl at T=(288.15-318.15)K

m_B **mol·kg^{-1}**	V_E^o $(\partial V_2^o/\partial T)_P$				
	288.15K	**298.15K**	**308.15K**	**318.15K**	$(\partial^2 V_2^o/\partial T^2)_P$
	Vit. C in water				
0.0	0.1509	0.1299	0.1089	0.0879	0.0053
Vit. C in water in LiCl					
0.1	0.1194	0.1109	0.1024	0.0939	-0.0008
0.25	0.1328	0.1268	0.1208	0.1148	-0.0006
0.5	0.1645	0.1395	0.1145	0.0895	-0.0025
1.0	0.0537	0.0881	0.1227	0.1569	0.0034

Conclusions

Partial molar volume at infinite dilution have been determined by linear regression analysis of the density and apparent molar volume data for Vit. C water and in aqueous solution of LiCl. The increase in V_2^o values with increase in temperature may be attributed to increase in solvation of Vit. C in aqueous and mixed aqueous LiCl solutions.

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Partial molar expansibilities have also been calculated. These values decrease regularly in water with temperature, but in LiCl these values decrease with temperature except at 1.0 m_B of LiCl. However, no regular fashion with increased LiCl molality have been observed.

The values of $(\partial^2 V_2^o/\partial T^2)_P$ been calculated for ascorbic acid in water and in all concentration of cosolute i.e. LiCl. The value of $(\partial^2 V_2^o/\partial T^2)_P$ for ascorbic acid in water is positive which suggest that ascorbic acid promote structure maker in aqueous media. In the presence of LiCl the value of $(\partial^2 V_2^o/\partial T^2)_P$ are negative at (0.1, 0.25, 0.5) m_B, which means ascorbic acid diminishes the structure of water at the said molalities. Whereas the positive values at 1.0 m_B LiCl gave the clue that ascorbic acid is structure promoter at this concentration.

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