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Viscometric Studies On Vitamin C in aqueous LiCl solution at T= (388.15-318.15)K

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Abstract

Viscosities of water soluble Vit.C in water and solutions of LiCl in water was measured at molalities; m_B = (0.1,0.25,0.5 and 1.0) at T = (288.15-318.15) K using Ubbelohde type capaliry viscometer. Jones-Dole equation have been used to calculate B-Coefficient values from relative viscosity data. The transfer values of B-coefficient and dB/dT derivative of B-coefficient was calculated from collected data. The obtained values of dB/dT are negative suggesting the structure-making nature of vit. C in aqueous LiCl solutions. The calculated $\Delta\mu_2^o$ values are positive and larger than $\Delta\mu_1^o$. ΔS and ΔH are positive for Vit. C in the cosolutes studied which advocate that the bond breaking and decrease in order is accompanied with the formation of the transition state. Further, Gibb's free energy value for Vit. C in aqueous LiCl solutions gave a clue that the formation of transition state is not appreciated in this system.

Introduction

Vitamins are highly required by living cells for the maintenance and regulating various biological functions in living system. [1]. Vitamins cannot be synthesized by human body, thus must be included in diet. Vit. C (L-Ascorbic acid) is water soluble vitamin. It is a white crystalline substance structurally resemblance to hexoses. Electrolyte is a substance which dissociate into free ions when dissolved in aqueous solutions to produce an electrically conductive medium. Major electrolytes of in body include the ions like sodium, magnesium, potassium, calcium, chloride, phosphate and bicarbonate.

Characterization of solution behavior of vitamins in aqueous and mixed aqueous solutions is essentialto understand the types of interactions occurring between solute and

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consulate in solutions phase. [2] Complexation equilibria of melt ions with relatively simple biomolecules such as amino acids, small peptides, vitamins, nucleic bases, nucleosides, and nucleotides provided useful model to understand the nature of metal-protein, metal-nucleic acid, metal-vitamin interactions occurring in biological systems. Therefore, the thermodynamic properties like partial molar volume, viscosity, heat capacity, compressibility etc. of vitamins have been of great interest to chemist due to their significant role in biological process. Viscosities and apparent molar volumes of various solutes and cosolutes are helpful in elucidating such interactions.

Attempts have been made from time to time by various workers to explore the solution behavior of Vit.C in various aqueous and mix aqueous solutions. Various physico-chemical properties which have been studied are apparent molal heat capacities, adiabatic compressibilities, apparent molal volumes and viscosities. However, as the present investigation deal with viscosity, so main stress is laid on viscosity which is briefly reviewed.

Ayranci et. Al [1] measured thermodynamic properties (partial molar volumes and compressibilities) of Vit. C in aqueous NaCl solutions at T= (283.15-313.15) K. The values of these properties were positive in water and in NaCl solutions. Complex interactions have been observed between Vit.C and NaCl in aqueous system.

Kaulgud et.al.[3] reported apparent molal volume (ϕ_v), apparent molal compressibility (ϕ_k) and B-coefficients of dilute aqueous solutions of ascorbic acid in 0.06m sodium chloride. The value of ϕ^o_k for ascorbic acid in aqueous solution appears to be slightly more negative than the value observed in NaCl solution. No significant differences in ϕ^o_v values are observed in aqueous and NaCl solutions of ascorbic acid. This suggest that

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ascorbic acid gives less protection to water in NaCl solution. Apelblat and Manzurola measured the the apparent molar volumes of Vit.C in water at 298.15 K. The ionization of Vit. C which is quite prominent phenomenon at low concentrations was ignored in this report [4]. Hakin et. al calculated the thermodynamic properties of Vit. C in water at T=(288.15 K-308.15) K. Ionization volume (ΔV^o) and ionization heat capacity (ΔCp^o) for these systems have been determined. Also the thermodynamic parameters for sodium salts of Vit. C have been calculated. [5]

Thermodynamic and transport properties are very sensitive towards solute-solute and solute-solvent interactions and thus provide excellent information about interaction in solutions. [6] In present study the solution behavior of Vit. C, in water and in aqueous of LiCl has been determined at temperatures 288.15 K, 298.15 K, 308.15 K, 318.15 K by measuring the viscosities of solutions in question. Ubbelohde type capillary viscometer was used to measure viscosity.. viscosity *B*-coefficient, and other related thermodynamic parameters have been calculated and collected data and attempt has been made to interpret the solute-cosolute-solvent interactions occurring in solution phase.

Experimental

Chemicals

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

Table 1 : Sources and Grades of Chemicals Used

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

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Before use, the chemicals were not further purified but were dried in the oven for 24 hours and then kept over the anhydrous $CaCl_2$ in a vacuum desiccator.

The details of the preparation of solutions, density meter, viscometer and their working have been discussed elsewhere [7-9].

Result and discussion

The relations used to calculate viscosities; η, is given below:

$$\eta/\rho = [at - (b/t)] \quad \ldots 5$$

In this relation ρ, t, a and b are density and flow time of the solutions, and, the viscometer constants respectively. The values of relative viscosities, η_r ($\eta_r = \eta/\eta_o$).Here η_o and η, represents the viscosities of solvent and solutions respectively) are given in Table 2. *B*-coefficients values have been calculated from η_r, and molarity; C as per Jones-Dole [10] equation as given below:

$$\eta_r = 1 + BC \quad \ldots 6$$

B-coefficient values are summarized in Table 2.

Table 2: C, η_r values of Vit. C in different solutions of LiCl at studied temperatures.

c (mol·l^{-1})	η_r	c (mol·l^{-1})	η_r	c (mol·l^{-1})	η_r
Ascorbic acid in Water					
T= 288.15K					
0.10111	1.0514	0.19940	1.0813	0.29704	1.1168
0.43668	1.1572	0.49852	1.2138	0.57557	1.2621
0.68453	1.3171	0.78190	1.3789		
T = 298.15 K					
0.10089	1.0276	0.19894	1.0704	0.29632	1.1163
0.43559	1.1648	0.49726	1.2067	0.5747	1.2651
0.68129	1.3072	0.77940	1.3617		
T = 308.15 K					

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0.10057	1.0348	0.19831	1.0741	0.29541	1.1155
0.43413	1.1625	0.49556	1.2056	0.57207	1.2556
0.67733	1.3009	0.77662	1.3485		
T = 318.15 K					
0.10018	1.0301	0.19666	1.0683	0.29170	1.1052
0.42741	1.1498	0.47740	1.1915	0.56448	1.2400
0.65100	1.2765	0.73816	1.3251		
T = 288.15 K $m_B = 0.1,\ \eta_o = 1.153$					
0.10289	1.0404	0.2830	1.0883	0.30345	1.1372
0.42370	1.1941	0.50631	1.2388	0.59874	1.2884
0.69720	1.3447	0.77890	1.4028		
$m_B = 0.25,\ \eta_o = 1.1621$cP					
0.10321	1.0581	0.20024	1.0965	0.30336	1.1440
0.38938	1.1847	0.50869	1.2386	0.60183	1.2914
0.69699	1.3491	0.79322	1.4109		
$m_B = 0.50,\ \eta_o = 1.203$cP					
0.10374	1.0559	0.20531	1.1024	0.3947	1.1490
0.40565	1.2019	0.49990	1.2618	0.58466	1.3079
0.70532	1.3491	0.77495	1.3977		
$m_B = 1.0,\ \eta_o = 1.265$cP					
0.10402	1.0603	0.20752	1.1109	0.30589	1.1524
0.41374	1.2099	0.49547	1.2567	0.61976	1.3120
0.69722	1.3440	0.79377	1.4363		
T = 298.15 K $m_B = 0.1,\ \eta_o = 0.907$cP					

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0.10263	1.0343	0.20784	1.0774	0.30276	1.1227
0.42258	1.1741	0.50475	1.2153	0.59651	1.2650
0.69398	1.3142	0.78009	1.3764		
m_B = 0.25, η_o = 0.917cP					
0.10297	1.0439	0.19976	1.0819	0.30261	1.1253
0.38938	1.1744	0.50721	1.2227	0.59982	1.2728
0.69419	1.3242	0.78924	1.3878		
m_B = 0.50, η_o = 0.952cP					
0.10350	1.0362	0.20485	1.0765	0.30890	1.1200
0.40523	1.1688	0.50002	1.2200	0.58576	1.2817
0.70741	1.3416	0.78096	1.4070		
m_B = 1.0, η_o = 0.989					
0.10377	1.0538	0.20702	1.0970	0.30518	1.1420
0.41287	1.2013	0.49457	1.2345	0.61909	1.2858
0.69693	1.3444	0.79429	1.4050		
T = 308.15 K **m_B = 0.1, η_o = 0.729**					
0.10232	1.0356	0.20720	1.0768	0.30183	1.1139
0.42140	1.668	0.50350	1.2057	0.59535	1.2493
0.69312	1.2992	0.77422	1.3525		
m_B = 0.25, η_o = 0.748					
0.10202	1.0362	0.19790	1.0575	0.29979	1.1054
0.38473	1.1555	0.50250	1.2147	0.59431	1.2704
0.69375	1.3127	0.79116	1.3580		

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m_B = 0.50, η_o = 0.758					
0.10164	1.0427	0.20420	1.103	0.30784	1.1353
0.40371	1.1751	0.49792	1.2163	0.58298	1.2529
0.70334	1.3132	0.77584	1.3608		
m_B = 1.0, η_o = 0.809					
0.10345	1.0433	0.20638	1.0819	0.30425	1.1297
0.41167	1.1777	0.49324	1.2125	0.61775	1.2667
0.69574	1.3251	0.79355	1.3791		
T = 318.15 K **m_B = 0.1, η_o = 0.729**					
0.10192	1.0369	0.20637	1.0758	0.30058	1.1137
0.41899	1.1626	0.50020	1.1971	0.59076	1.2425
0.68680	1.2841	0.76632	1.3317		
m_B = 0.25, η_o = 0.612					
0.10226	1.0376	0.19835	1.0772	0.30043	1.1162
0.38553	1.1551	0.50349	1.2022	0.59546	1.2564
0.68928	1.2932	0.78395	1.3431		
m_B = 0.50, η_o = 0.636					
0.10279	1.0364	0.20340	1.0749	0.30659	1.1152
0.40198	1.1651	0.49565	1.2060	0.58013	1.2510
0.69946	1.2873	0.77118	1.3464		
m_B = 1.0, η_o = 0.670					
0.10307	1.0450	0.2056	1.0784	0.30311	1.1171
0.41020	1.1693	0.49157	1.2031	0.61594	1.2515

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0.69397	1.3074	0.79203	1.3578		

m_B = molality of solvent (aqueous LiCl solutions) in mol·kg^{-1}
η_o = molality of solvent (aqueous LiCl solutions) in cP.

The viscosity *B*-coefficients of transfer, $\Delta_{tr}B$, from water to aqueous LiCl can be calculated as given below.

$\Delta_{tr}B$ = *B*-coefficients (in aqueous LiCl solutions–*B*-coefficients (in water)

. The plots of calculated $\Delta_{tr}B$ values versus different at m_B = (0.1,0.25,0.5,1.0) molality of $LiCl_2$ are shown in Fig. 1(m_B = molality of cosolute LiCl). These values increase with increase in concentration of LiCl and decrease with increase in temperature.

For ascorbic acid in LiCl, the $\Delta_{tr}B$ value increase sharply at 288.15 K but the $\Delta_{tr}B$ value almost show linear behavior at other temperatures i.e. (298.15 K, 308.15 K, 318.15 K). It may be noted that $\Delta_{tr}B$ values in case of LiCl decreases sharply from 288.15 K to higher temperatures 298.15 K to 318.15 K and remain almost constant at these temperatures.

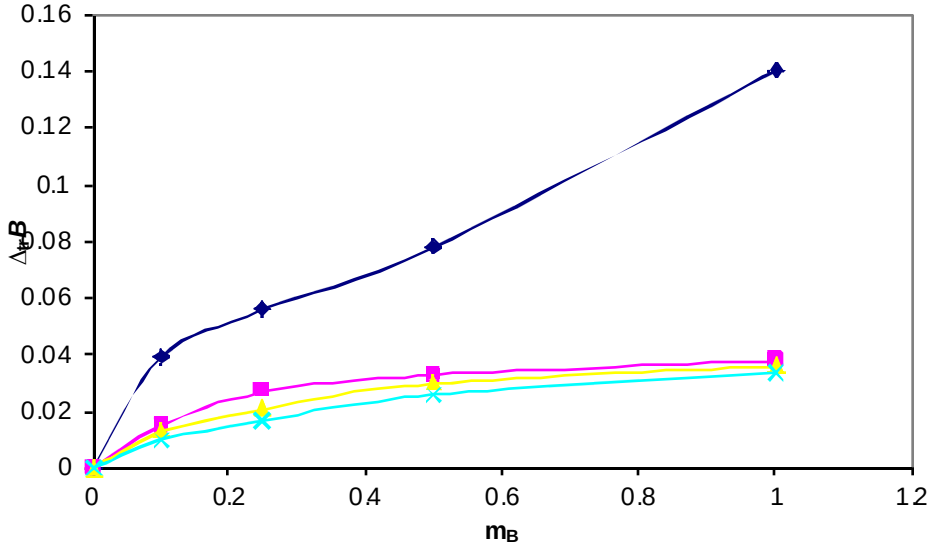

Fig.1 $\Delta_{tr}B$ vs m_B for Vit.C at temperatures (288.15 ♦, 298.15 ■, 308.15▲, 318.15 ×) K.

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The viscosity *B*-coefficients reflect the net structural effect of the charged groups and the hydrophobic groups on the solvent. The viscosity *B*-coefficient through light on the effect of philic or phobic groups present on solute or consulates, on water. So its values can be considered as measure of solute-solvent interactions in solution media. The obtained value of *B*-coefficients for the systems Vit.C and LiCl are given in Table 3**.** The in the values of viscosity *B*-coefficients increases with molality of LiCl suggests the increased structured solution media in the presence of added solutes.

Table 3: *B*-coefficients and *dB/dT* values of Vit. C in different solutions of LiCl at studied temperatures.

m_B (mol·kg^{-1})	$B \cdot 10^3$ (m^3·mol^{-1})				*dB/dT* (m^3·K^{-1}·mol^{-1})
	288.15K	**298.15K**	**308.15K**	**318.15K**	
0.10	1.721	1.780	1.212	1.310	-0.020
0.25	1.651	1.752	1.952	1.201	-0.015
0.50	1.431	1.512	1.711	1.910	0.026
1.00	1.189	1.218	1.385	1.589	-0.010

m_B = molality of solvent (aqueous LiCl solutions) in mol·kg^{-1}

The *dB/dT* is the temperature coefficient of viscosity coefficient-*B*. Its sign of, i.e., is important indicator for finding the effect of solute on structure of solutions, in comparison of B-coefficients. The calculated values for temperature coefficients *dB/dT* of Vit. C in aqueous LiCl solutions at studied temperatures are given in Table 3. Negative *dB/dT* of Vit. C in aqueous $LiCl_2$ solution classifies this vitamin as a structure-maker.

Erying,s equation [11] can be used to calculate activation free energy of various flow of a single solute in a free solvent $\Delta\mu_1^o$ as follows:

$$\eta_o = (hN_A/V_1^o) \exp(\Delta\mu_1^o/RT) \quad \ldots 7$$

in equation 7, symbols h, N_A, R have usual meaning and V_1^o is the average molar volume of solvent i.e. aqueous LiCl solutions. The calculated $\Delta\mu_1^o$ values in water and in (0.1, 0.25, 0.50 and 1.0) mol·kg^{-1} aqueous LiCl solutions are given in Table 4. The activation

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free energy of viscous flow, $\Delta\mu_2^o$ for solute Vit. C in solution of cosolute (LiCl solutions in present case) were evaluated by using Feakin's [11] relation which supplements Eyring transition-state theory as given below:

$$\Delta\mu_2^o = \Delta\mu_1^o + (RT/V_1^o)\,[1000B - (V_1^o - V_2^o)] \quad \ldots 8$$

The free-energy activation of viscous flow is a useful parameter to assess the complexity of liquid structure. The activation free energy, $\Delta\mu_2^o$ is an significant parameter to have an Idea about the structure of liquid, for ascorbic acid in aqueous solutions of LiCl at studied temperatures is give in Table 4. As is clear, $\Delta\mu_2^o$ are positive and much higher than $\Delta\mu_1^o$ (Table 4), indicating the lesser stability of transition state formation in the presence of Vit.C. The $\Delta\mu_2^o$ values for ascorbic acid in LiCl decreases with temperature and increases with increase in concentration which shows that the of transition state formation is less favored at higher studied temperature.

The entropies of activation , ΔS_2^o values can calculated from the slope of $\Delta\mu_2^o$ and T. The values of enthalpies of activation, ΔH_2^o and ΔS_2^o at studied molalities are given in Table 5.

$$\Delta H_2^o = \Delta\mu_2^o + T\Delta S \quad \ldots 9$$

In the present study both ΔS_2^o and ΔH_2^o are positive in LiCl solutions, which suggest that in the present case, breakage of bonds and decrease in order is accompanied with the formation of the transition .

According to the transition state theory, in molal solutions, each molecule of solvent and solution and passes through transition phase with in the solution.$\Delta\mu_2^o$ contain two contributers; the first one ΔG_2^o (1-1′) Gibb's free energy of transfer of solute from the ground to transition state of solvent and the movement of solute through its own

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viscous transition state, ΔG_2^o (2-2′) is the second contribution to $\Delta\mu_2^o$.The ΔG_2^o (1-1′) can be calculated from the following equation.

$$\Delta G_2^o \text{ (1-1′)} = \Delta\mu_2^o - \Delta G_2^o \text{ (2-2′)} \qquad \ldots 10$$

ΔG_2^o (2-2′) is equal to $\Delta\mu_1^o$. ΔG_2^o (1-1′) values are given in Table 5. The $\Delta\mu_2^o$ and ΔG_2^o (1-1′) values again are larger and positive than $\Delta\mu_1^o$, which indicating that the breaking and distortion of intermolecular bonds is accompanied in the formation of the transition state which is also a less favored process.

Table 4 : $\Delta\mu_1^o$ values of Vit. C in different solutions of LiCl at studied temperatures.

Temp (K)	m_B (mol.kg^{-1})	LiCl
288.15	0.00	9.44
	0.10	9.47
	0.25	9.49
	0.50	9.57
	1.00	9.70
298.15	0.00	9.16
	0.10	9.21
	0.25	9.23
	0.50	9.33
	1.00	9.43
308.15	0.00	8.9
	0.10	8.97
	0.25	9.24
	0.50	9.57
	1.00	9.70
318.15	0.10	8.73
	0.10	8.76
	0.25	8.80
	0.50	8.91
	1.00	9.05

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Table 5 : ΔG_2^o values of Vit. C in different solutions of LiCl at studied temperatures.

Temp (K)	m_B (mol.kg^{-1})	LiCl
288.15	0.00	70.71
	0.10	75.88
	0.25	76.77
	0.50	78.36
	1.00	79.31
298.15	0.00	69.72
	0.10	71.55
	0.25	72.76
	0.50	73.70
	1.00	74.28
308.15	0.00	66.70
	0.10	68.33
	0.25	69.48
	0.50	70.61
	1.00	71.09
318.15	0.10	64.64
	0.10	66.12
	0.25	66.70
	0.50	67.74
	1.00	65.54

Conclusions

Viscosities of Vit.C in aqueous LiCl solutions have been measured at T = (288.15-318.15) K using Ubbelohde type capaliry viscometer. Relative viscosity is used to calculate viscosity B-coefficient by fitting data in Jones-Dole equation. The negative values of *dB/dT* suggest that Vit. C in aqueous LiCl acts as structure-maker. The $\Delta\mu_2^o$ and ΔG_2^o (1-1′) values are larger and positive than $\Delta\mu_1^o$, which indicating that the

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breaking and distortion of intermolecular bonds is accompanied in the formation of the transition state which is also a less favored process.

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