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Study on Solution Behavior of Some Oxalate Salts in Aqueous Vitamin Solutions

Koyeli Das, Mahendra Nath Roy*

Department of Chemistry, University of North Bengal, Darjeeling - 734 013, West Bengal, India.

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ABSTRACT

The solubility of solids in vitamin C has much impact in cell metabolism on dissolution in water. Densities (ρ), viscosities (η), apparent molar volume, refractive index (n_D), of oxalate salts ($Li_2C_2O_4$, $Na_2C_2O_4$, $K_2C_2O_4$, $(NH_4)_2C_2O_4$) have been studied in (0.005, 0.02, 0.035, 0.05, 0.065, 0.08) mass fraction of ascorbic acid in water (H_2O) at 298.15 K, respectively. Masson equation has been employed to find the extent of interaction (solute-solvent interaction) in terms of the limiting apparent molar volume (φ_v^0) by extrapolating to zero concentration and experimental slopes (S_V^*) which interpreted the solute-solvent and solute-solute interactions, respectively, in the solutions. Using the Jones–Dole equation, the viscosity data were analyzed to determine the viscosity A and B-coefficient, which have also been interpreted the solute-solute and solute-solvent interaction, respectively, in the solutions. Molar refractions (R_M) have been calculated with the help of the Lorentz–Lorenz equation. The role of the solvent and the contribution of solute-solute and solute-solvent interactions to the solution complexes have also been analyzed through the derived properties. The Gibbs energies of mixing for $K_2C_2O_4$-vitamin-C binary solids and liquids and solid-saturated $K_2C_2O_4$-vitamin-C-H_2O ternary liquids were modeled using asymmetric Margules treatments.

Key words: *Solution chemistry, Thermodynamics, Apparent molar volume,·Molecular interaction, Solute-solute interaction, Oxalate salts, Ascorbic acid, Physico-chemical properties.*

1. INTRODUCTION

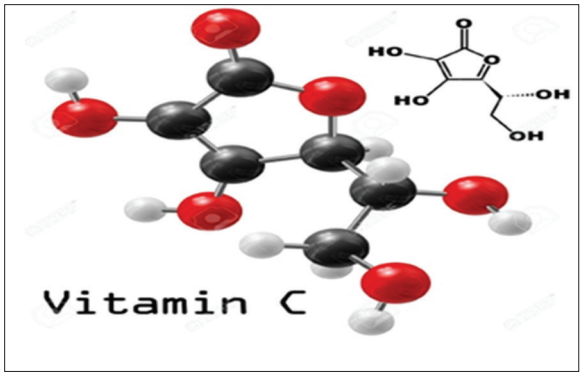
During the first third of the 20th century, a major focus of research in physiological chemistry was the identification of vitamins, compounds that are essential to the health of humans and other vertebrates but cannot be synthesized by these animals and must, therefore, be obtained in the diet. Early nutritional studies identified two general classes of such compounds: those soluble in non-polar organic solvents (fat soluble vitamins) and those that could be extracted from foods with aqueous solvents (water-soluble vitamins). Eventually, the fat-soluble group was resolved into the four vitamin groups A, D, E, and K, all of which are isoprenoid compounds synthesized by the condensation of multiple isoprene units. Vitamins are necessary precursors for various coenzymes [1-3]. We considered the fact that many enzymes require cofactors to be catalytically active. One class of these cofactors, termed coenzymes, consists of small organic molecules, and many of which are derived from vitamins. Vitamins themselves are organic molecules that are needed in small amounts in the diets of some higher animals. These molecules serve the same roles in nearly all forms of life, but higher animals lost the capacity to synthesize them in the course of evolution. For instance, whereas *Escherichia coli* can thrive on glucose and organic salts, human beings require at least 12 vitamins in the diet. The biosynthetic pathways for vitamins can be complex, and thus, it is biologically more efficient to ingest vitamins than to synthesize the enzymes required to construct them from simple molecules. This efficiency comes at the cost of dependence on other organisms for chemicals essential for life. Indeed, vitamin deficiency can generate diseases in all organisms requiring these molecules [2,3]. The body needs vitamin C, also known as ascorbic acid or ascorbate, to remain in proper working condition. Vitamin C benefits the body by holding cells together through collagen synthesis; collagen is a connective tissue that holds muscles, bones, and other tissues together. Vitamin C also aids in wound healing, bone and tooth formation, strengthening blood vessel walls, improving immune system function, increasing absorption and utilization of iron, and acting as an antioxidant. Vitamin C works with vitamin E as an antioxidant, and plays a crucial role in neutralizing free radicals throughout the body. An antioxidant can be a vitamin, mineral, or a carotenoid, present in foods, that

*Corresponding Author:
E-mail: mahendraroy2002@yahoo.co.in

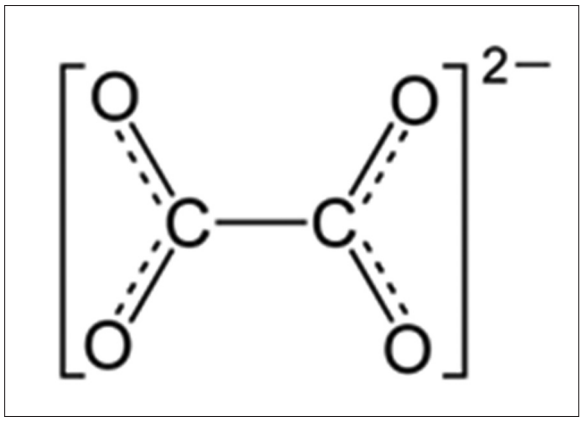
slows the oxidation process and acts to repair damage to cells of the body. Studies suggest that vitamin C may reduce the risk of certain cancers, heart disease, and cataracts. Research continues to document the degree of these effects. The molecular structure of ascorbic acid is depicted in Scheme 1.

Oxalates are a common food chemical. They are indigestible to humans and for the most part should stay in the gastrointestinal track and pass through unabsorbed. A healthy gut will resist absorbing them and will contain bacteria that break down oxalates to further protect the body. No benefit has been found to oxalates in the body. In fact, they disrupt normal body functions on the cellular level. Once absorbed, the body needs to protect itself from them, either by putting them somewhere in storage or by excreting them. Oxalate (IUPAC: ethanedioate) is the dianion with the formula C_2O_42-, also written $(COO)_22-$. Either name is often used for derivatives, such as salts of oxalic acid, for example $Na_2C_2O_4$, $K_2C_2O_4$, $Li_2C_2O_4$, $(NH_4)_2C_2O_4$ are used in the work. The molecular structure of oxalates is depicted in Scheme 2.

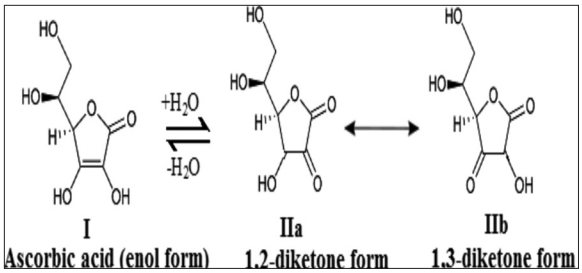
The strong understanding of solubility in aqueous solutions affords the opportunity to compare empirical mixture models with traditional thermodynamic models to determine if there is any physical meaning behind the coefficients and to determine the most efficient way to use mixture models. The soluble concentration of constituents in solution can change significantly when crossing phase boundaries. This principal can be demonstrated with the $Na_2C_2O_4$-$C_6H_8O_6$-H_2O, $K_2C_2O_4$-$C_6H_8O_6$-H_2O, $Li_2C_2O_4$-$C_6H_8O_6$-H_2O, $(NH_4)_2C_2O_4$-$C_6H_8O_6$-H_2O system, referred here in (Scheme 3,4,5). In extension of our earlier study [4-8], we have attempted to ascertain the nature of solute-solvent/co-solute interactions of vitamins (ascorbic acid) in w_1 = 0.005, 0.02, 0.035, 0.05, 0.065, and 0.08 mass fraction of aqueous solution at 298.15 K, respectively, as literature survey reveals



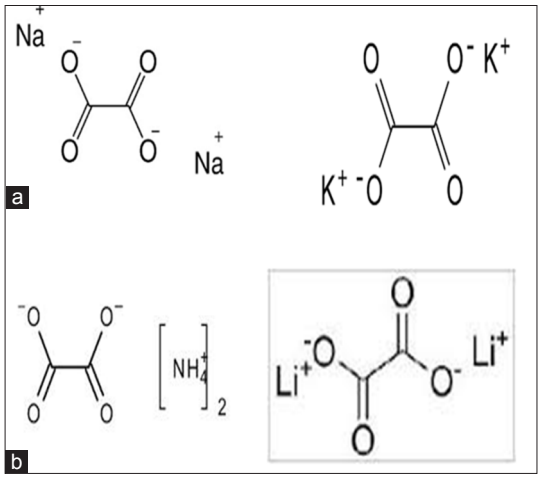
Scheme 1: Molecular structure of ascorbic acid.



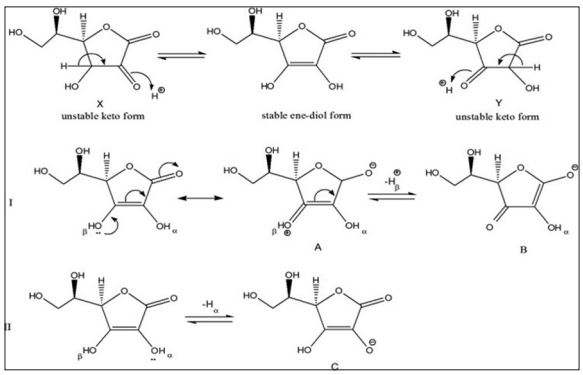
Scheme 2: Pictorial representation of oxalate ion.



Scheme 3: Keto-enol tautomerism of ascorbic acid.



Scheme 4: Pictorial representation of the four oxalate salts, (a) Sodium oxalate, (b) potassium oxalate, (c) ammonium oxalate, (d) lithium oxalate.



Scheme 5: The stability of the conjugate base of ascorbate ion.

that no work has been carried out in such simple ternary systems. We have attempted to report the limiting apparent molar volume (φ_v^0), experimental slopes (S_V^*), viscosity B-coefficients, molar refraction (R_M) according to the variation in the equilibrium of three-component systems.

2. EXPERIMENTAL

2.1. Source

$Li_2C_2O_4$, $Na_2C_2O_4$, $K_2C_2O_4$, $(NH_4)_2C_2O_4$ were purchased from Sisco Research Laboratories (SRL Pvt. Ltd. Bombay, India), whereas L-ascorbic acid ($C_6H_8O_6$) was purchased from SRL (S.D. Fine – Chem Ltd., Mumbai, India). The mass purity of salts was ≥0.99. The salts were dried from moisture at 353 K for 48 h, and then they were cooled and store in desiccators before use.

2.2. Apparatus and Procedure

Initially, we attempted to measure the solubility of the salts by dissolving them in aqueous binary solution of vitamins. Binary solvent mixtures were prepared by mixing a required volume of ascorbic acid and H_2O with earlier conversion of required mass into volume at 298.15, 303.15, and 308.15 K using experimental densities. A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion of molarities into molality was accomplished using experimental density values. All solutions were prepared fresh before use. The uncertainty in molality of the solutions is evaluated to ±0.0001 mol kg^{-3}. The Mettler Toledo AG-285 was used to measure the masses of the respective oxalates and ascorbic acid. The densities of the solutions (ρ) were measured by means of vibrating-u-tube Anton Paar digital density meter (DMA 4500M) with a precision of 0.00005 $g.cm^{-3}$ at the desired temperature. It was calibrated by measuring the density of double-distilled water and dry air and then comparing the density values with the standard reference value given by the certificate of density standard liquids.

The viscosity was also measured with a Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 fitted to a Brookfield Digital Bath TC-500. The viscosities were obtained using the following equation:

$$\eta = (100/RPM) \times TK \times torque \times SMC \quad (1)$$

Where, RPM, TK (0.09373) and SMC (0.327) are the speed, viscometer torque constant and spindle multiplier constant, respectively. The instrument was calibrated against the standard viscosity samples supplied with the instrument, water and aqueous $CaCl_2$ solutions. Temperature of the solution was maintained within ±0.01°C using Brookfield Digital TC-500 temperature thermostat bath. The viscosities were measured with an accuracy of ±1%. Each measurement reported herein is an average of triplicate reading with a precision of 0.3%.

Refractive index was measured with the help of a Digital Refractometer Mettler Toledo. The light source was a light-emitting diode, λ=589.3 nm. The refractometer was calibrated twice using distilled water, and calibration was checked after every few measurements. The uncertainty of refractive index measurement was ±0.002 units.

Volumetric properties are useful tools in studying the solution behavior of solutes and reveal valuable information about solute-solvent-cosolute interactions. They include apparent molar volume, apparent molar expansion which is derivative of volume with respect to temperature.

3. RESULTS AND DISCUSSION

The physical properties such as densities, viscosities, refractive index of simple oxalates in different mass fractions (w_1 = 0.005, 0.02, 0.035, 0.05, 0.065, 0.08) of aqueous vitamin C mixture at 298.15, 303.15, 308.15 K as a function of concentration (molality) are listed in Table 1.

Uncertainty of density measurement: ±0.00005 g cm^{-3}, Uncertainty of viscosity measurement: ±0.02 mPa s, Uncertainty of refractive index measurement: ±0.002 units.

3.1. Density

The density (ρ) which is a measure of solute-solvent interactions can be attributed as increase of density with concentration indicates the increase in solute-solvent interactions, whereas the decrease in density indicates the lesser magnitude of solute-solvent interactions. Increase in density with concentration is due to the shrinkage in the volume which in turn is due to the presence of solute molecules. As observed in (Tables 2 and 3) an increasing trend of density values

Table 1: Mass-fraction of solvent mixture.

w_1	Temperature	$\rho.10^{-3}/kgm^{-3}$		η/mPa s		n_D	
		Experimental	Literature	Experimental	Literature	Experimental	Literature
w_1=0.1	298.15 K	1.004491	-	105.84	-	1.3359	-
	303.15 K	1.002766	-	106.34	-	-	-
	308.15 K	1.001083	-	107.07	-	-	-

may be interpreted to the structure-making behavior of the solvent due to the added solute.

3.2. Apparent Molar Volume

Apparent molar volumes, ϕ_V, were determined from the measured densities of solvent ρ_0 and of solution, ρ, using the following equation:

Table 2: Solubility tested.

Samples taken	In water	n methanol	Solution used (vitamin C+H_2O)
Li - Oxalate	Soluble	Insoluble	Soluble
Na - Oxalate	Sparingly	Insoluble	Soluble
K - Oxalate	Completely	Insoluble	Soluble
NH_4 - Oxalate	Completely	Insoluble	Soluble

$$\phi_V = M_2/\rho - [1000\ (\rho-\rho_0)/(m\rho\rho_0)] = M_2/\rho - [1000\ (\rho-\rho_0)/(c\rho_0)] \quad (1)$$

Where, ρ_0 and ρ are densities of solvent and solution, respectively, m is the molality, c is the molarity of the solution and M_2 is the molecular weight of the solute, oxalates. The solvent was taken as 0.1 M ascorbic acid solution for oxalate salts. For the determination of ϕ_V of vitamins in the presence of oxalates, the solvent was taken as the solution containing H_2O, at 0.1 M and oxalates at various molalities.

Apparent molar volumes at infinite dilution, were determined by extrapolating the plot of ϕ_V versus concentration to zero concentration. For ascorbic acid, being a non-electrolyte, in water, this extrapolation was made on the basis of the following empirical equation:

Table 3: Experimental values of densities (ρ), refractive index (n_D) of oxalates in different mass fraction of aqueous ascorbic acid at temperatures, T=298.15 K and at ambient pressure.

T/K	Systems	M/mol kg^{-1}	$\rho.10^{-3}$/kg m^{-3}	n_D
298.15 K	I	w_1=0.1		
	H_2O+ascorbic acid+Li-Ox	0.005	1.00522	1.3327
		0.02	1.00603	1.3331
		0.035	1.00721	1.3336
		0.05	1.00827	1.334
		0.065	1.00892	1.3343
		0.08	1.00976	1.335
298.15K	II	w_1=0.1		
	H_2O+ascorbic acid+Na-Ox	0.005	1.00494	1.333
		0.02	1.00652	1.333
		0.035	1.00796	1.333
		0.05	1.00949	1.334
		0.065	1.01176	1.335
		0.08	1.01237	1.335
298.15 K	III	w_1=0.1		
	H_2O+ascorbic acid+K-Ox	0.005	1.00403	1.333
		0.02	1.00503	1.333
		0.035	1.00597	1.333
		0.05	1.00729	1.333
		0.065	1.00744	1.334
		0.08	1.00884	1.334
298.15 K	IV	w_1=0.1		
	H_2O+ascorbic acid+NH_4-Ox	0.005	1.00428	1.333
		0.02	1.00515	1.334
		0.035	1.00616	1.333
		0.05	1.00737	1.335
		0.065	1.00786	1.335
		0.08	1.00116	1.337

[a]Uncertainty of the molality u(m)=0.0002 mol kg^{-1}, density u(ρ)=0.00005×10^{-3} kg m^{-3}, viscosity u(η)=0.01 mPa s, refractive index u(n_D)= 0.0002

Table 4: Data of $(\eta/\eta^0-1)/m^{1/2}$ obtained from the viscosity calculations of oxalates at different temperatures.

Molality	25°C	30°C	35°C
I			
0.005	4.388	2.232	0.144
0.02	4.876	3.163	1.010
0.035	5.160	3.375	1.309
0.05	5.552	3.766	1.734
0.065	5.410	2.064	1.761
0.08	4.267	2.232	2.308
II			
0.005	1.860	0.906	0.744
0.02	2.139	1.178	0.930
0.035	2.250	1.233	1.406
0.05	2.294	1.261	2
0.065	1.238	1.609	1.857
0.08	1.581	1.586	1.721
III			
0.005	1.302	8.485	5.439
0.02	1.488	9.050	6.935
0.035	1.828	10.049	5.859
0.05	1.941	11.449	7.138
0.065	1.857	4.314	4.525
0.08	1.907	4.030	3.467
IV			
0.005	0.172	3.163	0.964
0.02	0.086	3.535	1.044
0.035	0.065	3.797	2.551
0.05	3.108	3.883	2.591
0.065	2.822	3.199	2.139
0.08	2.630	3.163	2.169

$$\phi_V = \varphi_v^0 + S_V^* \, m^{1/2} \quad (2)$$

Where, S_V^* is an experimentally determined parameter. Linear regression analysis of the plot of ϕ_V versus square root of m provided both φ_v^0 and S_V^* parameters. Extrapolation according to Equation (2) assumes ascorbic acid to be a non-electrolyte. In other words, the effect of the small extent of hydrolysis of ascorbic acid on ϕ_V values was assumed to be negligible. Table 4 shows that the values of ϕ_V are large and positive for the systems, suggesting strong solute-solvent interactions. The apparent molar volumes ϕ_V were calculated from the measured densities through Equation (1). They were plotted against the square root of the molar concentrations ($m^{½}$) of ascorbic acid and then the data were regressed linearly according to equations. To determine apparent molar volumes at infinite dilution, (φ_v^0), and the experimental slopes (S_V^*) were determined using least squares fitting of the ϕ_V values to the Masson equation. Ascorbic acid behaves as a vinylogous carboxylic acid wherein the double bond transmits electron pairs between the hydroxyl group and the carbonyl. There are two resonating structures for the deprotonated form, differing in the position of the double bond. The deprotonated form is an enolate which is usually strongly basic. Ascorbic acid also converts into two unstable diketone tautomers by proton transfer, although it is the most stable in the enol form. The proton of the enol is lost and re-acquired by electrons from the double bond to produce diketone. There are two possible forms: 1,2-diketone and 1,3-diketone (IIa and IIb) [4]. The molecule exists in equilibrium with two ketone tautomers, which are less stable than the enol form. In solutions, these forms of ascorbic acid rapidly interconvert (Scheme 6,7,8).

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 and mixed aqueous solutions. 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. The solvation behavior of a solute has been studied by most important parameters, i.e., apparent molar volume ϕ_V. In this study, the apparent molar volume, ϕ_V of vitamin C in water at different temperatures were determined from density measurements [5-7].

It is known that the salts of oxalates remain dissociated in solutions as shown in (Scheme 2,3,4). On dissociation of any of this, proton ascorbate ion will be formed [6,7]. The stability of the conjugate base (respective ascorbate ion) will determine the acidity of the respective proton (Scheme 5).

Ascorbic acid (stable enediol form) on dissociation of Hα proton gives its conjugate base structure "C." On the other hand, enol form of ascorbic acid (I) on dissociation of Hβ proton gives its conjugate base "B" which on resonance can reconvert to "A." As structure "B" has one more equally contributing resonating structure "A," whereas structure "C" does not have any resonating structure. Therefore, the stability of conjugate base generated on removal of Hβ proton is more than that of conjugate base generated on removal of Hα proton. Thus, β proton of ascorbic acid is more acidic than α proton as each dissociation is more facile. Therefore, the negatively charged oxygen atoms in oxalate ion of the salts probably interacts with the most acidic hydrogen (β hydrogen)

of enol form of ascorbic acid rendering higher solute-solute interaction as evident from (φ_v^0) values. The solubility of ionic compounds (salts) depends on the solute-solute versus solute-solvent interactions [5-8]. If the solute-solvent interactions are stronger than the solute-solute interactions, the salt will be soluble in that solvent. Solubility chart of the oxalate salts is listed as shown in Table 2.

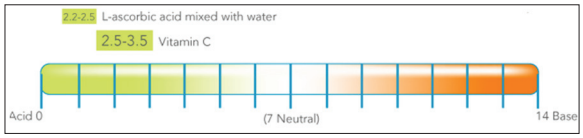
The order of solute-solvent interaction mentioned in (Tables 2-6). The more stronger evidence can be given on the basis of the (φ_v^0) values, that it is large and positive in magnitude, for sodium oxalate, in the entire composition range of water + ascorbic acid at 298.15 K, thereby showing the presence of strong ion-solvent interactions, due to the favorable Hard-Hard interaction but not combination. Evidence can be given by noting that sodium has the capacity to get bonded with the oxalate both in the monobasic and dibasic

Table 5: Measurement of viscosity (η) in centipoises at 298.15, 303.15, 308.15 K, respectively.

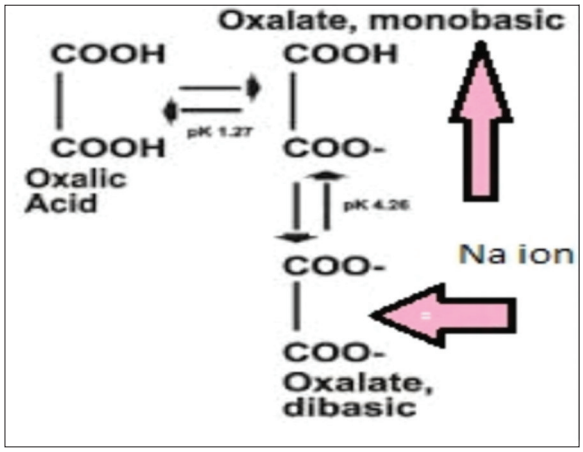
Composition	298.15 K	303.15 K	308.15 K
I			
0.005	0.76	0.88	0.99
0.02	0.98	1.1	1.12
0.035	1.14	1.24	1.22
0.05	1.30	1.4	1.36
0.065	1.38	1.16	1.42
0.08	1.28	1.24	1.62
II			
0.005	0.83	0.80	0.72
0.02	0.92	1.14	1.03
0.035	1.02	1.44	1.09
0.05	1.09	1.78	1.35
0.065	1.12	1.05	1.12
0.08	1.17	1.07	1.03
III			
0.005	0.86	0.83	0.8
0.02	0.99	0.91	0.86
0.035	1.08	0.96	0.96
0.05	1.15	1	1.10
0.065	1.00	1.1	1.12
0.08	1.10	1.13	1.13
IV			
0.005	0.89	0.93	0.94
0.02	1.25	1.14	1.01
0.035	1.36	1.30	1.30
0.05	1.39	1.42	1.39
0.065	1.41	1.38	1.36
0.08	1.43	1.44	1.42

state within the range of pK~4.26. The pH scale of the ascorbic acid in water is shown in Scheme 6.

Hence, together sodium oxalate along with ascorbic acid forms ascorbate at pK~−0.86 probably leads to the firm interactions shown in Schemes 7 and 8.



Scheme 6: pH ranges of interactions of aqueous ascorbic acid solutions.



Scheme 7: Probable interaction pattern of the studied system.

Table 6: Examining viscosity A, B-coefficients of lithium, sodium, potassium, ammonium oxalates at 298.15-308.15 K, respectively.

Systems	A-coefficient			B-coefficient		
	25°C	30°C	35°C	25°C	30°C	35°C
I	3.844	1.620	0.53	7.387	9.726	10.14
II	0.955	0.682	0.061	4.396	18.59	8.229
III	1.685	0.780	0.033	2.896	2.339	7.942
IV	1.5	0.835	0.115	15.14	4.876	12.22

Table 7: Limiting apparent molar volumes (φ_v^0), experimental slopes (S_V^*) of lithium oxalate, sodium oxalate, potassium oxalate, ammonium oxalate in aqueous ascorbic acid at 298.15 K.

Salt	$\varphi_v^0 \times 10^6$ ($m^3\ mol^{-1}$)	$S_V^* \times 10^6$ ($m^3\ mol^{-3/2} kg^{1/2}$)
Lithium oxalate	73.23	−123.5
Sodium oxalate	173.2	−219.7
Potassium oxalate	125.4	−195.4
Ammonium oxalate	113.5	−180.2

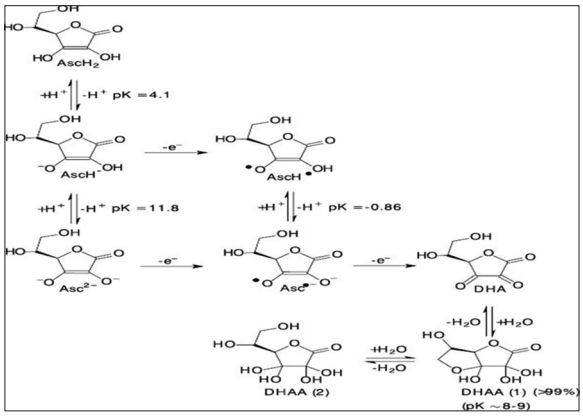
Table 8: Molality (m), apparent molar volume (ϕ_v), molar refraction (R) of lithium oxalate, sodium oxalate, potassium oxalate, ammonium oxalate in aqueous vitamin C solution in different mass fraction at room temperature.

m/mol.kg^{-1}	Systems	$\varphi_v \times 10^6$ (m^3 mol^{-1})	R (cm^3 mol^{-1})
w_1=0.1	I		
0.005	H_2O+ascorbic acid+Li-Ox	63.5965	20.8182
0.02		55.0596	20.8345
0.035		52.0636	20.8404
0.05		46.8147	20.8444
0.065		43.9422	20.8451
0.08		35.0847	20.8486
w_1=0.1	II		
0.005	H_2O+ascorbic acid+Na-Ox	156.992	27.4277
0.02		148.532	27.3846
0.035		125.752	502.106
0.05		118.627	501.699
0.065		125.752	500.927
0.08		109.908	500.625
w_1=0.1	III		
0.005	H_2O+ascorbic acid+K-Ox	112.99	34.0514
0.02		99.40156	34.0175
0.035		83.21324	7227.86
0.05		83.09953	7208.93
0.065		76.1566	7201.7
0.08		72.18996	7181.73
w_1=0.1	IV		
0.005	H_2O+ascorbic acid+NH_4-Ox	104	25.418
0.02		84.45691	25.4652
0.035		77.21768	25.3705
0.05		75.9117	25.4781
0.065		67.56527	25.4657
0.08		64.21171	25.7749

Table 7 also shows the value of φ_v^0 decreases for the individual solute of lithium and ammonium thereby showing that the ion-solvent interactions decrease due to the hindrances during polarization. A quantitative comparison of φ_v^0 values shows that these are much larger in magnitude than those of S_V^* values for all the solutes. This suggests that ion-solvent interactions dominate over the ion-ion interactions in water + ascorbic acid mixtures in 298.15 K. The decrease in the values suggests that the pair wise interaction is restricted by the interaction of the interacting group of one molecule to side chain of the other vitamins molecules. The values of the vitamin solution given in Table 7 decreases with increase in the interactive centers solvent medium due to the size factors interpreting the minimum solute-solute interaction which also suggest the presence of cation-anion penetration which occurs due to competition between ions to occupy the void space of the large solvent molecules [9-15]. Therefore, an appreciable interionic penetration occurs, and these give rise to a negative slope (i.e., weak ion-ion interaction and strong ion-solvation) in the ϕ_V versus ($m^{1/2}$) for these solutes. The increase in may be attributed to the increase in solvation [14,15]. A plausible mechanism of interaction between aqueous ascorbic acid, different oxalates is mentioned in Scheme 9 shows the trend as $I_B > I_C > I_D > I_A$.

3.3. Viscosity Calculation

The viscosity data has been analyzed using Jones–Dole equation [1-15].



Scheme 8: Probable mechanism of the studied system.

$(\eta/\eta_0-1)/m^{1/2} = A + Bm^{1/2}$

Where, η_0 and η are the viscosities of the solvent and solution, respectively. A and B are the experimental constants known as viscosity A and B-coefficient projected by a least-squares method and are reported in Table 6, which are specific to solute-solute and solute-solvent interactions, respectively. The values of A and B-coefficients are estimated by plotting $(\eta/\eta_0-1)/m^{1/2}$ against $\sqrt{m}$ reported in Table 4,7,8. The values of the A-coefficient are found to decrease in all the samples, but exceptionally increase steadily with the increase in temperature in the sodium oxalate; these results indicate the presence of very weak solute-solute interactions in all the samples and much stronger solute-solvent interactions in sodium individual. These results are in excellent agreement with those obtained from S_V^* values discuss earlier [1-15]. The effects of solute-solvent interactions on the solution viscosity can be inferred from the B-coefficient. The viscosity B-coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 6, it is evident that the values of the B-coefficient are positive, thereby suggesting the presence of strong solute-solvent interactions, and strengthened with an increase the temperature as shown in the lithium, potassium, and ammonium salts in Table 4,6-8. The higher B-coefficient values for higher viscosity values is due to the solvated solutes molecule associated by the solvent molecules all round to the formation of associated molecule by solute-solvent interaction, would present greater resistance, and this type of interactions are strengthened with a rise in temperature. While in the case of sodium oxalate, the B-coefficient irrespective of the other oxalates been sampled is found to decrease significantly with the variance in temperature and the A-coefficient showed a sudden increase in values, thereby showing the reverse characteristics.

3.4. Refractive Index Calculation

The molar refraction, R can be evaluated from the Lorentz-Lorenz relation:

$R = \{(-1)/(+2)\}\ (M/\rho)$

Where R, n_D, M and ρ are the molar refraction, the refractive index, the molar mass, and the density of solution, respectively. The refractive index of a substance is defined as the ratio c0/c, where c is the speed of light in the medium and c0 the speed of light in vacuum. Stated more simply, the refractive index of a compound describes its ability to refract light as it moves from one medium to another, and thus, the higher the refractive index of a compound, the more the light is refracted. As stated by Deetlefs *et al*. The refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser and with the increase of the mass fraction of ascorbic acid in solvent mixture refractive index value also increases [3-14]. Hence a perusal of Tables 3 and 8, we found that the refractive index and the molar refraction values, respectively, are higher for potassium and sodium compared to other two oxalates, indicating the fact that the molecules are more tightly packed in the mixture. The slope increases along with the uniformity. The interaction in the solution is basically solute-solvent interaction and a small amount of solute-solute interaction [16-24]. This is also good agreement with the results obtained from density and viscosity parameters discussed above. The trend in the package of the studied oxalates in the aqueous mixture of ascorbic acid is:

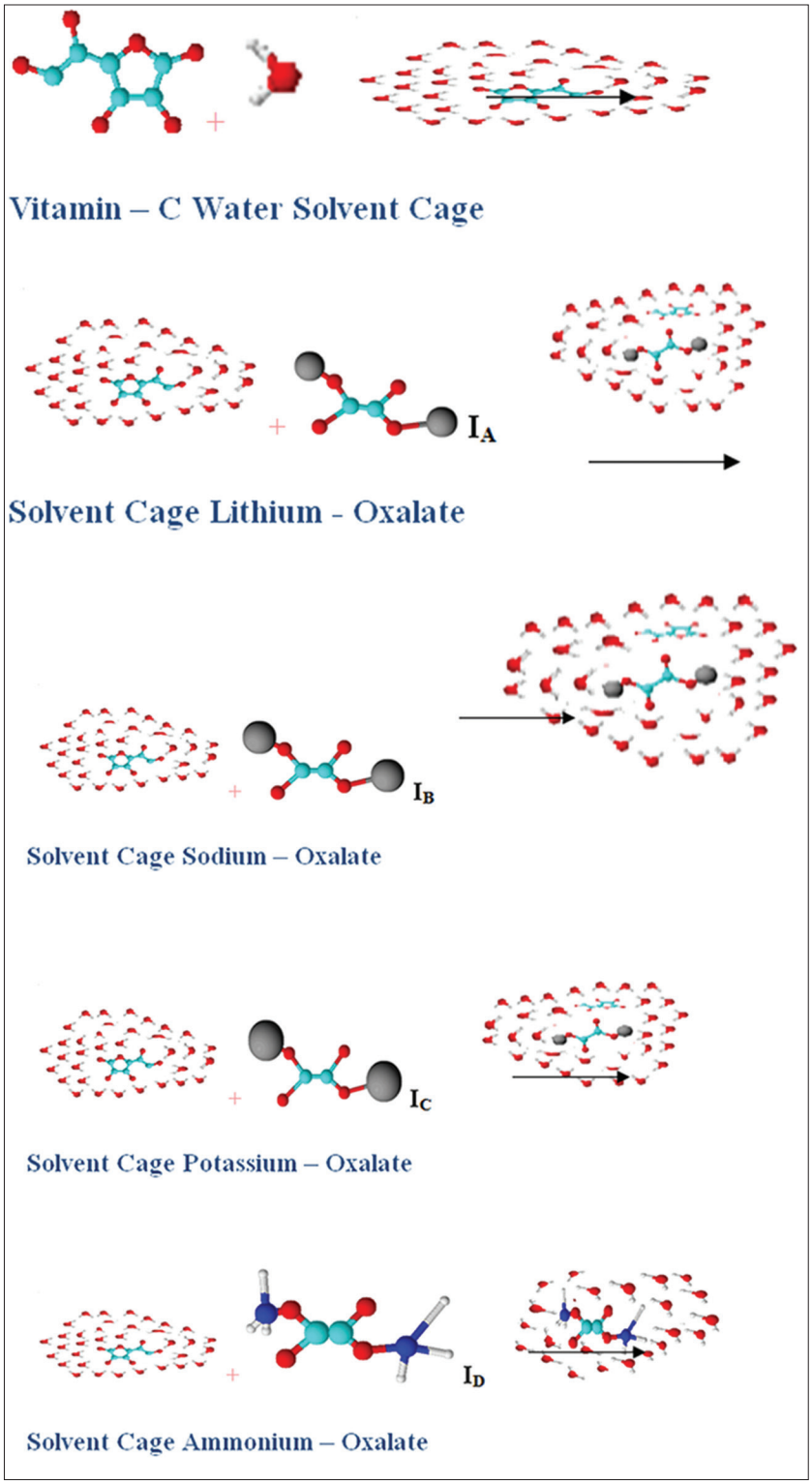
$K_2C_2O_4$[III] > $NA_2C_2O_4$[II] > $(NH_4)_2C_2O_4$[IV] > $Li_2C_2O_4$[I].

3.5. The $K_2C_2O_4$-Ascorbic acid-Water Ternary System

The phase rule is the relationship between the number of phases, P, the number of components, C and the number of degrees of freedom, F of a system at equilibrium at a given P and T. The rule is P+F = C+2, where 2 stands for the intensive variables pressure, P and temperature, T. This is a general rule applicable to all types of reactive and non-reactive systems. The solubility and density of the equilibrium liquid phase for the ternary $K_2C_2O_4$ + ascorbic acid + H_2O system were determined experimentally at 298.15 K, two solid phases were formed in the ternary $K_2C_2O_4$ + ascorbic acid + H_2O system that correspond to $K_2C_2O_4$-H_2O and $K_2C_2O_4$-$C_6H_8O_6$ at 298.15 K. The phase diagrams of the system could be constructed based on the measured solubility [25-27]. The binary system $K_2C_2O_4$-ascorbic acid has a bigger crystallization field than either $K_2C_2O_4$-H_2O or the mixture. The solubilities of $K_2C_2O_4$-H_2O and $K_2C_2O_4$- ascorbic acid increase slightly with increasing temperature while the crystalline region of the compound $K_2C_2O_4$-ascorbic acid decreases as the temperature increases.

4. CONCLUSION

A portray of the thermophysical and thermodynamic impression of the aqueous ascorbic acid solution



Scheme 9: The schematic representation of solute-solvent interaction, for the studied oxalates in aqueous vitamins binary mixtures.

in accordance with the inorganic oxalate salts were studied. It is specified from the values of the density, limiting apparent molar volume (φ_v^0), viscosity *B*-coefficients, molar refraction (R_M), and the presence of phases. The refractive index and the molar refraction values imply that ascorbic acid molecules are more tightly packed in the solution leading to higher solute-solvent interaction than the other vitamins. In summary, viscosity B-coefficient values for oxalates indicate the presence of strong

solute-solvent interactions, and these interactions are further strengthened at higher temperatures and higher concentrations of ascorbic acid in binary solutions. The conclusions from experimental and derived parameters also provide important working function of the ascorbic acid with oxalates in biological systems, which demands the uniqueness of the work.

5. ACKNOWLEDGMENT

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****Bibliographical Sketch***

Dr. Mahendra Nath Roy is a Professor of Physical Chemistry and Program Coordinator of SAP, DRS-III in the University of North Bengal, Darjeeling. His research interests are in the areas of host-guest inclusion complexes, ionic liquids, solution thermodynamics, and polymer chemistry. His contribution has been recognized by a large number of high impact research articles (Total - 192, International - 141 and National - 51) and books (Total - 4, International - 01 and National - 03). He is the life member of ICS, ISC, CRSI, and JTR. He has been awarded one-time grant amounting Rs.7.00 lac by UGC, New Delhi under basic scientific research (BSR) as he has singly produced nineteen (19) Ph.D. students. He has also received "Prof. Suresh C. Ameta Award" from Indian Chemical Society, Kolkata.

Miss. Koyeli Das obtained first class in her M.Sc. degree in Physical Chemistry from University of North Bengal in the year 2014 and is currently working under the fellowship RGNFD with Prof. Mahendra Nath Roy, as a researcher, Department of Chemistry, NBU. She has attended many seminars and conferences and highlighted her research work.