Protonation Equilibria at Elevated Temperatures and Investigations on Thermodynamics Parameters for Ascorbic Acid at an Ionic Strength of 1.0 mol·dm^{-3} $NaClO_4$

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The protonation equilibria for ascorbic acid at an ionic strength of 1.0 mol·dm^{-3} $NaClO_4$ medium have been studied pH-potentiometrically. The protonation constants of ascorbic acid and the thermodynamic functions (ΔG, ΔH, and ΔS) for the successive and overall protonation processes of ascorbic acid have been derived at three different temperatures. A detailed thermodynamic analysis of the effects of temperature and ascorbic acid concentration influencing the protonation processes is presented and discussed to determine the factors which control these processes.

Introduction

Ascorbic acid has special importance since it is found naturally in a wide variety of plants and animals, and it plays a vital role in nearly all chemical and biological processes. The oxidation of ascorbic acid (vitamin C) is a very important redox reaction, as it has interesting biological properties. It is also a powerful reductant.[1] It is sensitive to heat and light and readily oxidizes by reacting with oxygen in the atmosphere.[2] Ascorbic acid is an essential nutrient in human diets and is necessary to maintain connective tissue and bone. Its biologically active form is vitamin C. Ascorbic acid is an electron donor for enzymes involved in collagen hydroxylation, biosynthesis of carnitine and norepinephrine, tyrosine metabolism, and amidation of peptide hormones. The ability of vitamin C to donate electrons also makes it a potent water-soluble antioxidant that readily scavenges free radicals such as molecular oxygen, superoxide, hydroxyl radical, and hypochlorous acid. Several mechanisms could account for a link between vitamin C and heart disease. One is the relation between LDL (low-density lipoprotein) oxidation and vitamins C and E. Vitamin C in vitro can recycle vitamin E, which can donate electrons to prevent LDL oxidation in vitro.

Ascorbic acid is also used in the nuclear industry as a decontaminating agent and reducing agent. In the cooling circuits of nuclear reactors, layers of radioactive contaminants such as activated corrosion products are formed on the surfaces of the cooling circuit components. With the increasing age of nuclear power stations, this leads to an increase in the activity of longer-lived nuclides. With the increasing age of the nuclear reactor, more frequent maintenance works are carried out. During such work the reactor components need to be decontaminated prior to the execution of maintenance. This is required to reduce occupational exposure. For the purpose of decontamination, various formulations like a combination of ascorbic acid and piconilic acid or ascorbic acid and ethylenediaminetetraacetic acid (EDTA) have been used. These acids were used after mainly considering the chemistry between the carboxylic acids, the nature of the contaminants, and the chemical form of the structural material on which the contaminants are deposited. Therefore, for effective decontamination without affecting the structural materials, the chemical interactions of these carboxylic acids with the structural materials as well as the contaminants need to be known. The purpose of this investigation is, therefore, to determine the protonation constants of ascorbic acid and study their equilibria at various temperatures at an ionic strength of 1.0 mol·dm^{-3} $NaClO_4$.

Despite its recognized importance, there are only a few experimental contributions on the acid−base behavior and thermodynamic properties of ascorbic acid. A search of the literature showed that studies on the thermodynamic protonation constants of ascorbic acid using a variety of experimental and theoretical tools have been few.[3,4] No systematic work seems to have been done on the determination of the protonation constants at different temperatures or measurement of the thermodynamic parameters. Knowledge of the thermodynamic properties of ascorbic acid is of great interest for the decoding of the mechanism of bidentate ligand dissociation and for revealing the influence of the nature of the solvent and hydrophobicity. The protonation constants are important for environmental scientists, chemical engineers, chemists, and specialists in related fields as these alter the reactivity, spectral properties, physical behavior, and solubility. The information is also of great interest for the nuclear industry as it is being used as a decontaminating agent for coolant channels[5] as well as being used as an excellent reducing agent for plutonium.[6] It is known that the reactions of ascorbic acid with metal ions of constituents of coolant channels are important for corrosion studies that are yet to be fully elucidated. The exposition of the various phenomena in the coolant channel systems requires the protonation constants of ascorbic acid and its stability constants with constituent metal ions of coolant channels.

A pH metric method was used for the calculation of the protonation constants. The effects of ascorbic acid concentration and temperature on the protonation constants have been determined at an ionic strength of 1.0 mol·dm^{-3} ($NaClO_4$). The advanced software program HYPERQUAD[7] was used for the calculation of the protonation constants and distribution of species (H_2L, HL, L) at an equilibrium state.

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Table 1. Experimentally Measured *E*/mV as a Function of Alkali Volume *V*/cm³ for Glass Electrode Calibration and Protonation Titration at 298 K

Glass Electrode Calibration Titration[a]					
V	*E*	*V*	*E*	*V*	*E*
cm³	mV	cm³	mV	cm³	mV
0.00	289.1	3.37	257.1	5.67	−296.5
0.28	287.2	3.64	252.4	5.81	−301.6
0.68	284.5	3.90	247.1	6.02	−307.9
1.09	281.7	4.18	239.8	6.28	−313.7
1.43	279	4.45	230.2	6.55	−318.5
1.72	276.5	4.73	214.1	6.82	−322.3
2.01	273.9	5.00	174.3	7.10	−325.4
2.33	270.7	5.21	−251.8	7.45	−328.8
2.59	267.8	5.29	−267.2	7.86	−332.1
2.85	264.6	5.42	−281.9		
3.10	261.3	5.55	−290.3		
Protonation Titration[b]					
0.00	214.1	3.07	121.7	6.35	−247.20
0.13	206.4	3.33	116	6.49	−250.90
0.27	198.1	3.59	109.9	6.66	−255.60
0.39	191.6	3.81	104.40	6.81	−259.20
0.52	185.5	4.02	98.50	6.96	−262.80
0.66	179.9	4.16	94.00	7.14	−266.60
0.79	174.9	4.31	88.70	7.34	−270.50
0.92	170.7	4.46	82.80	7.57	−274.60
1.05	166.6	4.60	75.40	7.81	−278.60
1.18	162.8	4.83	59.50	8.11	−283.20
1.34	158.9	4.98	39.10	8.41	−287.50
1.47	155.4	5.14	−51.60	8.72	−291.60
1.63	151.4	5.30	−170.80	8.87	−293.40
1.82	147.2	5.45	−198.30	9.17	−297.10
1.99	143.9	5.60	−214.50	9.43	−299.90
2.18	139.7	5.75	−224.80	9.82	−304.10
2.41	135.1	5.89	−230.80	10.28	−308.40
2.63	131.0	6.04	−237.70	10.77	−312.90
2.85	126.2	6.19	−242.30	11.30	−317.00

[a] Initial volume of titer: 10 cm³; titer: $HClO_4$: 0.504 mmol; titrant: NaOH concentration: 0.104 mol·dm^{-3}; background ionic strength: 1.0 mol·dm^{-3}; temperature: 298 K. [b] Initial volume of titer: 10 cm³; titer: ascorbic acid: 0.510 mmol; titrant: NaOH concentration: 0.104 mol·dm^{-3}; background ionic strength: 1.0 mol·dm^{-3}; temperature: 298 K; E^0: 405.0 mV; slope factor: 1.0.

Table 2. Experimentally Measured *E*/mV as a Function of Alkali Volume *V*/cm³ for Glass Electrode Calibration and Protonation Titration at 313 K

Glass Electrode Calibration Titration[a]					
V	*E*	*V*	*E*	*V*	*E*
cm³	mV	cm³	mV	cm³	mV
0.00	295.7	5.03	162.8	5.57	−277.6
2.70	272.8	5.05	151.4	5.69	−284.4
3.75	256.7	5.06	128.2	5.88	−292.2
4.01	251.2	5.08	2.2	6.12	−299.2
4.23	244.8	5.09	−121.7	6.56	−308.5
4.43	237.7	5.13	−179.5	6.93	−314.0
4.57	231.2	5.16	−202.7	7.40	−319.3
4.67	225.5	5.19	−219.8	8.31	−326.5
4.76	218.6	5.22	−229.0	9.06	−330.9
4.88	205.5	5.25	−237.8	11.27	−339.5
4.98	186.5	5.30	−249.8	14.79	−347.0
5.00	177.6	5.36	−258.5	16.63	−349.2
5.02	171.4	5.45	−268.5		
Protonation Titration[b]					
0.00	216.8	4.77	59.2	6.13	−230.8
0.11	209.9	4.81	55.3	6.30	−238.9
0.20	203.5	4.88	48.5	6.58	−251.6
0.31	197.3	4.93	41.9	6.71	−255.1
0.42	191.2	4.97	35.2	6.91	−261.1
0.54	185.1	5.01	29.9	7.27	−266.0
0.67	179.6	5.04	20.8	7.57	−272.4
0.86	172.7	5.08	9.7	7.98	−280.7
1.06	166.3	5.10	−3.7	8.25	−285.1
1.34	158.4	5.11	−11.8	8.61	−290.2
1.67	150.1	5.12	−15.3	8.94	−294.8
1.85	145.9	5.14	−39.7	9.47	−301.2
2.10	140.4	5.15	−42.5	9.96	−306.1
2.38	134.3	5.18	−66.7	10.52	−311.3
2.59	129.7	5.22	−94.4	11.09	−315.9
2.91	123.1	5.26	−99.2	11.67	−320.2
3.18	116.9	5.29	−100.7	12.80	−325.8
3.47	110.1	5.32	−104.5	13.36	−330.2
3.66	105.1	5.35	−108.2	14.57	−335.6
4.00	95.4	5.46	−139.7	16.19	−341.0
4.20	88.8	5.55	−161.7	19.83	−348.2
4.33	83.5	5.65	−184.8	25.02	−354.7
4.45	78.2	5.78	−201.2	31.94	−359.0
4.61	70.0	5.91	−212.1	33.03	−359.0
		6.02	−222.8		

[a] Initial volume of titer: 10 cm³; titer: $HClO_4$: 0.504 mmol; titrant: NaOH concentration: 0.104 mol·dm^{-3}; background ionic strength: 1.0 mol·dm^{-3}; temperature: 313 K. [b] Initial volume of titer: 10 cm³; titer: ascorbic acid: 0.505 mmol; titrant: NaOH concentration: 0.104 mol·dm^{-3}; background ionic strength: 1.0 mol·dm^{-3}; temperature: 313 K; E^0: 405.0 mV; slope factor: 1.0.

Experimental Section

Reagents. Analytical grade, vacuum-dried, ascorbic acid was dissolved in water to prepare 0.1 mol·dm^{-3} and 0.2 mol·dm^{-3} solutions, and an appropriate amount of $NaClO_4$ was added to adjust the ionic strength to 1 mol·dm^{-3}. The solution was prepared freshly each time and deaerated, and the container was covered with black paper to protect the solution from light. A standardized solution of analytical reagent grade sodium perchlorate was used for maintaining ionic strength. The NaOH solution was prepared at a concentration of 0.1 mol·dm^{-3}, and a calculated amount of $NaClO_4$ was added so as to get the final ionic strength of the solution at 1.0 mol·dm^{-3}. It was standardized against dried potassium hydrogen phthalate.

Apparatus. The potentiometric titrations were performed using an ORION 940 pH meter coupled to a personal computer through an RS-232 serial port for data acquisition. A combination glass electrode (ORION-910600) was used for the potentiometric measurements. The electrode response can be read to the third decimal place in terms of pH units with a precision of ± 0.001 and the potential with a precision of ± 0.1 mV. A thermostat "Meta-Lab" was used for maintaining the required temperature with a precision of ± 0.1 °C. A Teflon stirring bar was used for homogenizing the solution, and an inert atmosphere was maintained by continuously flushing air with dry nitrogen during the titration. A Mettler balance was used for weighing chemicals for the preparation of experimental solutions and buret weights during titrations. Titrations were done on a weight basis for better accuracy. As the software, employed for computation, required data to be input in volume units, these weights were converted into volumes using solution density.

Procedure. Each set of experiments essentially contains two steps, and they are the following:

(i) Calibration of the pH electrode: The calibration of the pH electrode is an important step as it ensures the response of the electrode. The value of the formal electrode potential, E^0, was obtained every time by Gran's method of titrating strong acid $HClO_4$ with strong alkali NaOH under the experimental conditions.

(ii) Determination of pK_a: Titration of ascorbic acid against standard NaOH was performed under similar experimental

Table 3. Experimentally Measured *E*/mV as a Function of Alkali Volume *V*/cm³ for Glass Electrode Calibration and Protonation Titration at 333 K

Glass Electrode Calibration Titration[a]					
V/cm³	*E*/mV	*V*/cm³	*E*/mV	*V*/cm³	*E*/mV
0.00	319.2	5.20	184.0	5.69	−252.5
2.78	294.5	5.22	165.5	5.77	−257.1
3.77	278.3	5.24	145.0	6.01	−267.8
4.02	273.7	5.26	−117.8	6.16	−272.4
4.25	267.6	5.29	−176.2	6.59	−280.5
4.51	258.3	5.32	−199.3	6.91	−286.0
4.70	249.6	5.36	−215.3	7.20	−289.7
4.86	238.8	5.39	−223.6	7.68	−294.5
4.96	231.9	5.45	−230.8	8.23	−299.0
5.04	222.4	5.51	−236.6	9.20	−305.4
5.11	210.4	5.55	−241.1	10.01	−308.1
5.16	199.7	5.63	−247.8	12.15	−315.4
Protonation Titration[b]					
0.00	236.1	4.32	99.1	6.58	−229.0
0.11	228.7	4.43	94.0	6.80	−236.5
0.25	220.3	4.56	86.7	7.01	−242.2
0.39	212.7	4.69	77.2	7.21	−246.9
0.56	205.7	4.77	69.7	7.48	−252.9
0.70	199.8	4.89	54.3	7.79	−256.8
0.87	193.8	5.02	21.9	8.13	−263.0
1.03	188.5	5.04	18.0	8.54	−268.7
1.25	181.7	5.05	15.0	9.11	−276.0
1.50	174.9	5.07	6.2	9.61	−281.2
1.69	169.8	5.08	−2.9	10.07	−285.0
1.97	163.1	5.10	−10.6	11.04	−293.0
2.21	157.4	5.13	−32.6	11.56	−296.0
2.65	147.1	5.17	−41.2	12.80	−303.5
2.91	141.1	5.21	−48.4	14.39	−310.0
3.14	135.7	5.29	−56.6	16.37	−314.9
3.32	131.3	5.30	−58.2	19.54	−321.0
3.58	124.4	5.49	−81.2	23.12	−325.9
3.73	120.0	5.91	−88.3	27.64	−330.7
3.91	114.7	6.19	−211.0	33.31	−333.3
4.04	110.2	6.31	−216.5		
4.18	105.0	6.44	−223.4		

[a] Initial volume of titer: 10 cm³; titer: $HClO_4$: 0.504 mmol; titrant: NaOH concentration: 0.104 mol·dm^{-3}; background ionic strength: 1.0 mol·dm^{-3}; temperature: 333 K. [b] Initial volume of titer: 10 cm³; titer: ascorbic acid: 0.505 mmol; titrant: NaOH concentration: 0.104 mol·dm^{-3}; background ionic strength: 1.0 mol·dm^{-3}; temperature: 333 K; E^0: 405.0 mV; slope factor: 1.0.

conditions as those employed during the calibration stage. For the pK_a determination, an experimental solution of 10 cm³ containing ascorbic acid in a 1.0 mol·dm^{-3} $NaClO_4$ ionic medium was titrated against standard NaOH of the same ionic strength. The titrations were carried out with two different concentrations ((0.1 and 0.2) mol·dm^{-3}) of ascorbic acid so as to know the concentration effect, if any on the measurements. The weights of the titrant added, and the resultant potentials/pH were recorded and stored in the computer. From the acquired data, the protonation constants for the two successive dissociations of ascorbic acid have been calculated using a software program.

Each experiment which includes steps (i) and (ii) was performed at three different temperatures, (298, 313, and 333) K, and two different ascorbic acid concentrations, to evaluate the thermodynamic parameters by measuring the pK_a values. The total time taken for each titration was around 2.5 h.

Results and Discussion

Protonation Constants. Ascorbic acid is a lactone with a 2,3-endiol group. The enolic group imparts acidity to the molecule which is at positions 2 and 3. The protonation equilibria of ascorbic acid can be expressed as

$$H^+ + A^{2-} \rightleftharpoons HA^-$$

$$2H^+ + A^{2-} \rightleftharpoons H_2A$$

and the corresponding protonation constants for above equilibria are given by

$$\beta_1 = \frac{[HA^-]}{[H^+][A^{2-}]} \text{ and } \beta_2 = \frac{[H_2A]}{[H^+]^2[A^{2-}]}$$

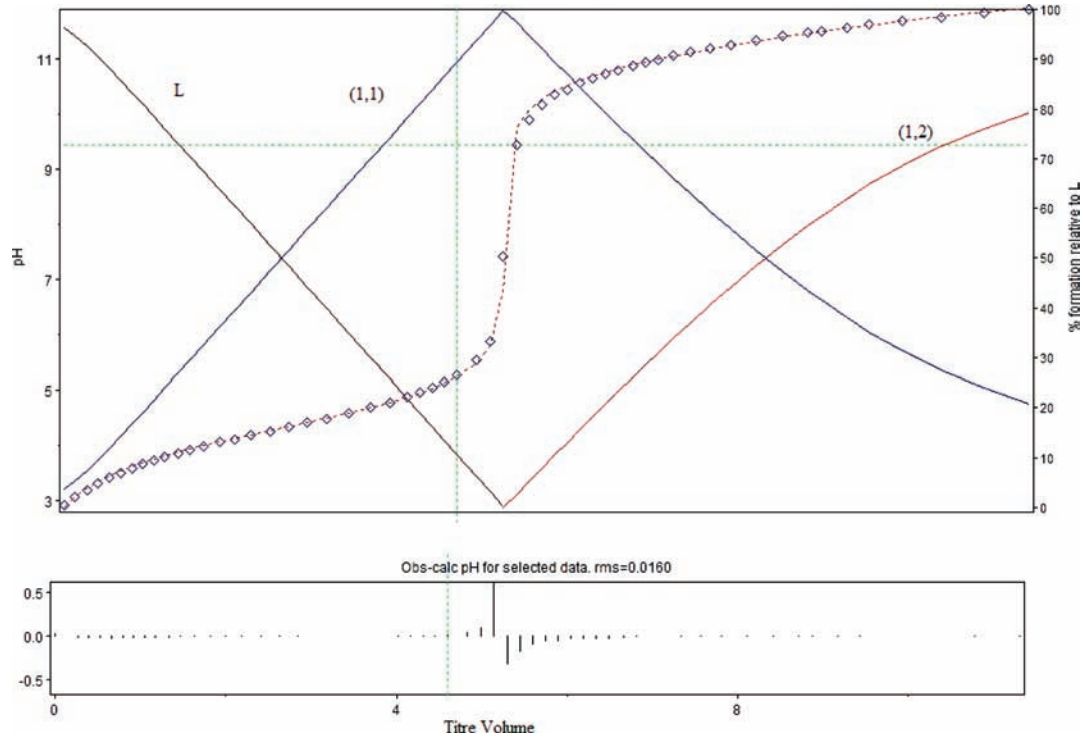


Figure 1. Typical titration curve of ascorbic acid (HYPERQUAD output). Left *y*-axis is scaled for titration curve; right *y*-axis is scaled for % formation curves. Titration curve has symbols (experimental points) and dotted line (HYPERQUAD calculated curve). Error scatter of the minimized function is given by *V*/cm^{-3} vs $pH^{observed} - pH^{calculated}$. Species (1,1) and (1,2) are HA^- and H_2A, respectively.

Table 4. Protonation Constants of Ascorbic Acid at (298, 313, and 333) K at an 1.0 mol·L^{-1} Ionic Strength of $NaClO_4$ and Related Thermodynamic Parameters

	temperature				
set no.	°C	log β_1	log β_2	log K_1	log K_2
I	25	11.35	15.38	11.35	4.03
II	25	11.37	15.55	11.37	4.18
III	25	11.35	15.56	11.35	4.21
IV	25	11.33	15.67	11.33	4.33
V	25	11.36	15.62	11.36	4.26
VI	25	11.37	15.59	11.37	4.22
mean		11.36 ± 0.03	15.56 ± 0.21	11.36 ± 0.03	4.20 ± 0.17
I	40	10.84	14.87	10.84	4.03
II	40	10.72	14.68	10.72	3.96
III	40	10.87	14.89	10.87	4.02
IV	40	10.80	14.88	10.80	4.09
mean		10.81 ± 0.09	14.83 ± 0.15	10.81 ± 0.09	4.02 ± 0.06
I	60	10.36	14.24	10.36	3.88
II	60	10.34	14.30	10.34	3.96
III	60	10.34	14.30	10.34	3.96
mean		10.35 ± 0.01	14.28 ± 0.04	10.35 ± 0.01	3.93 ± 0.05
		Stepwise Equilibrium Reactions			
thermodynamics	$H^+ + A^{2-} \rightleftharpoons HA^-$	$\Delta G_1 = -63.8 \pm 6.4$ kJ·mol^{-1}	$\Delta H_1 = -54.5 \pm 5.5$ kJ·mol^{-1}	$\Delta S_1 = 33.9 \pm 3.4$ J·mol^{-1}·K^{-1}	
	$H^+ + HA^- \rightleftharpoons H_2A$	$\Delta G_2 = -23.1 \pm 5.8$ kJ·mol^{-1}	$\Delta H_2 = -14.5 \pm 3.6$ kJ·mol^{-1}	$\Delta S_2 = 31.4 \pm 7.9$ J·mol^{-1}·K^{-1}	

Table 5. Literature Values of Protonation Constants of Ascorbic Acid in $NaClO_4$ Medium

medium strength	temperature			
mol·dm^{-3}	°C	log K_1	log K_2	ref
3	25		4.38	8
3	25		4.36	9
3	25	11.34	4.37	10
2	25		4.11	11
1	25	11.36	4.20	present work
1	40	10.81	4.02	present work
1	60	10.35	3.93	present work
1	25	10.90		12
1	25		3.95	13
1	10		4.08	13
1	25		4.03	14
1	6		4.16	14
1	35		3.89	14
0.5	25	11.1		12
0.5	25		4.11	13
0.2	25	11.73	4.16	15
0.1	25		4.02	11
0.1	25	11.3		12
0.15	25	10.35	3.96	16
0	25	11.5		12

The stepwise protonation equilibria of ascorbic acid can be expressed as

$$H^+ + A^{2-} \rightleftharpoons HA^-$$

$$H^+ + HA^- \rightleftharpoons H_2A$$

and the corresponding protonation constants for above equilibria are given by

$$K_1 = \frac{[HA^-]}{[H^+][A^{2-}]} \quad \text{and} \quad K_2 = \frac{[H_2A]}{[H^+][HA^-]}$$

pH titrations in duplicate were performed at temperatures (298, 313, and 333) K for the calibration of the glass electrode and determination of the protonation constants with varying concentrations of ascorbic acid. Titration details and experimental data for single titrations are listed in Tables 1, 2, and 3 respectively for temperatures at (298, 313, and 333) K.

For computation of protonation constants from pH titration data, an advanced software program HYPERQUAD 2006[7] was used. This software facilitates visual interpretations of refinement which in turn helps greatly in obtaining the best fit. A typical pH titration curve with experimental points and program fitted line is shown in Figure 1.

The protonation constants of ascorbic acid determined in the present work at three different temperatures are listed in Table 4. It is seen from the Table 4 that the protonation constant values differ very marginally by varying ascorbic acid concentrations, whereas the $-\log \beta$ values decrease with an increase in temperature, indicating that the dissociation of ascorbic acid increases with temperature.

The literature values of the protonation constants of ascorbic acid in perchlorate medium along with values obtained in the present work reported are compiled in Table 5. The values obtained in the present work at 298 K do not differ to a large extent from the literature values. Table 5 also indicates that no systematic work has been reported in the literature for protonation constants and thermodynamic parameters of ascorbic acid at elevated temperatures.

Thermodynamics Calculations. Thermodynamic parameters were calculated using protonation constants at elevated temperatures using the van't Hoff equation. The van't Hoff equation in chemical thermodynamics relates the change in temperature (T) to the change in the equilibrium constant (K) and gives

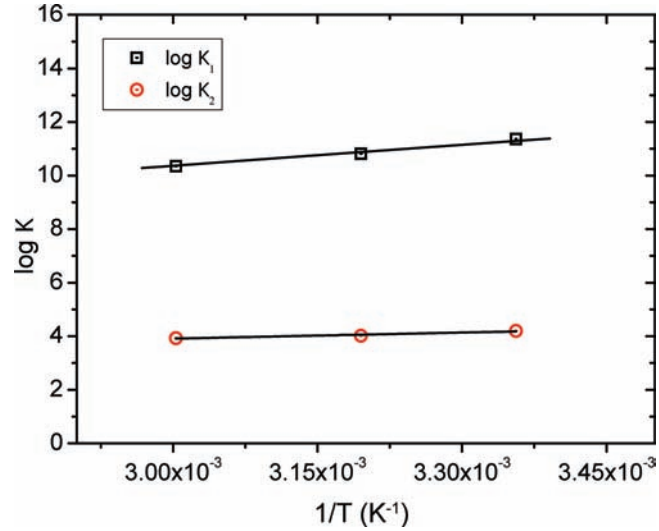


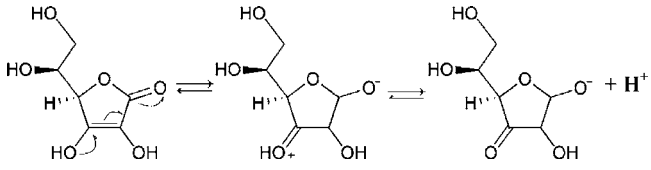
Figure 2. Plot of log β vs $1/T$ (K^{-1}).

the enthalpy change (ΔH) for the process. If the enthalpy change of reaction is assumed to be constant with temperature, the definite integral of the van't Hoff differential equation between temperatures T_1 and T_2 is given by

$$\ln\left(\frac{K_1^{T_2}}{K_1^{T_1}}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{or} \quad \ln K_1 = \frac{-\Delta H_1}{RT} + \frac{\Delta S_1}{R}$$

where $K_1^{T_1}$ is the stepwise equilibrium constant at absolute temperature T_1 and $K_1^{T_2}$ is the stepwise equilibrium constant at absolute temperature T_2. Therefore, the slope of the line, the natural logarithm of the equilibrium constant versus the reciprocal temperature, gives $\Delta H/R$, and the intercept gives $\Delta S/R$.

A plot of the logarithms of the protonation constants (log K) versus the reciprocal of temperature (K) is given in Figure 2, and the thermodynamic parameters calculated using the slope and intercept are included in Table 4. The ΔH and ΔS values determined in the present work for the two protonation equilibria are (−54.5 and −14.5) kJ·mol^{-1} and (33.9 and 31.4) J·mol^{-1}·K^{-1}, respectively. The free energy changes accompanied with the first and second protonation of ascorbic acid indicate that the protonation of one of the groups of 2,3-enediol moiety (ortho- or meta-positions from C1 carbonyl group) conjugated with the C1 carbonyl group is more favorable as compared to the other one. Conversely, the deprotonation should favor the other enol group. The electron transfer leading to the first deprotonation of ascorbic acid as shown below indicates that the enol at the meta position to the carbonyl group (position 3) is more amenable to deprotonation as compared to the enol group at position 2 (ortho to carbonyl).



Successive protonation, on the other hand, should proceed to favor the ortho position and then the meta position (2 followed by 3). These thermodynamic values also indicate that the protonation reactions are both enthalpy- as well as entropy-stabilized and the deprotonated form is strongly basic. The experimental thermodynamic values have been made available for the first time.

Literature Cited

(1) Carr, C.; Frei, B. Towards a new recommended dietary allowance for vitamin C based on antioxidant and health effects in humans. *Am. J. Chem. Nutr.* **1999**, *69*, 1086.
(2) Michael, B.; Davies; Austin, J.; Patridge, D. A. *Vitamin C: its chemistry and biochemistry*; Royal society of chemistry: London, 1991.
(3) Powell, K. J. *The IUPAC Stability Constant data bases*; Academi Software: Yorks, U.K., 2006.
(4) Smith, R. M.; Martel, A. E. *NIST, Scientific and Technical databases*; NIST: Department of Chemistry, College Station, TX, 2004.
(5) *Chemical Decontamination of the Primary Heat Transport (PHT) system of MAPS-2*; NuPower bulletin; NPCIL: Mumbai, India, 1999; Vol. 13, p 1.
(6) Newton, T. W. *The kinetics of the oxidation-reduction ractions of uranium, neptunium, plutonium and americium in aqueous solutions*; Report: IID-26506; Los Alamos Scientific Laboratory: Los Alamos, NM, 1975.
(7) Gans, P. *HYPERQUAD*; Protonic Software: Hanau, Germany, 2006. The suite of software programs was acquired from Depts. of Inorganic and Structural Chemistry, University of Leed, LS2 9JT, U.K. Gans, P.; Sabatini, A.; Vacca, A. Investigation of equilibria in solution. Determination of equilibrium constants with the HYPERQUAD suite of programs. *Talanta* **1996**, *43*, 1739.
(8) Ulmgren, P.; Wahlberg, O. Equilibrium studies of L-Ascorbate ions. IX. Equilibrium between iron(II) ions, Ascorbate ions and protons in 3M (Na)ClO_4 medium. *Acta Chem. Scand.* **1974**, *A28*, 631.
(9) Ulmgren, P.; Wahlberg, O. Equilibrium studies of L-Ascorbate ions. IV. Equilibrium between cadmium (II) ions, Ascorbate ions and protons in perchlorate self medium; and V. Cadmium ascorbate complexes in self medium containing 3M (Na, Cd)ClO_4 and ascorbic acid. *Acta Chem. Scand.* **1971**, *25*, 1064–1079.
(10) Wahlberg, O. Equilibrium studies of L-Ascorbate ions. III. Equilibrium between cadmium(II) ions, Ascorbate ions and protons in 3M (Na)ClO_4 medium. *Acta Chem. Scand.* **1971**, *25*, 1045.
(11) Hasegawa, Y.; Sugawara, T.; Choppin, G. Thermodynamic parameters of complexation of lanthanoid(III) with ascorbic acid. *Inorg. Chim. Acta* **1988**, *143*, 277–280.
(12) Martinez, P.; Zuluga, J.; Kraft, J.; van Eldik, R. Kinetics and mechanism of the oxidation of L-ascorbic acid by trisoxalatocobaltate(III) in basic aqueous solution. *Inorg. Chim. Acta* **1988**, *146*, 9–12.
(13) Kimura, M.; Yamamoto, M.; Yamabe, S. Kinetics and mechanism of the oxidation of L-ascorbic acid by tris(oxalato)cobaltate(III) and tris(1,10-phenanthroline)iron(III) complexes in aqueous solution. *J. Chem. Soc., Dalton Trans.* **1982**, 423.
(14) Pelizzetti, E.; Mentasti, E.; Pramauro, E. Kinetics and mechanism of the oxidation of ascorbic acid by tris(1,10-phenanthroline) iron(III) and its derivatives in aqueous acidic perchlorate media. *Inorg. Chem.* **1976**, *15*, 2898–2900.
(15) Kriss, E.; Kurbatova, G. *Zh. Neorg. Khim.* **197621**, (1302), 2368.
(16) Cape, J. N.; Cook, D. H.; Williams, D. R. Thermodynamic considerations in co-ordination Part XIX. In vitro studies of complexing equilibria involved in oral iron(II) therapy. *J. Chem. Soc., Dalton Trans.* **1974**, 1849.

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