Study of the Composition and Model Parameters of Complexes Formed in Fe(II)-Fe(III)-Ascorbic Acid-Water Systems

Jahongul Davlatshoeva[*], Mubashira Rakhimova, Gulrukhsor Eshova

Tajik National University, Dushanbe, Tajikistan

[*]kfk1964@mail.ru

Abstract. The redox system Fe(II)-Fe(III)-ascorbic acid-water at 298.16 K and 0.5 mol/l solution ionic strength was studied by the Clark-Nikolsky redox potential method. It was found that five complexes of Fe(III) composition are formed in the system: $[Fe(HAsc)]^{2+}$; $[Fe(HAsc)]^{+}$; $[Fe^{II}Fe^{III}(HAsc)_2(OH)_2]^{+}$; $[FeAsc]^{+}$; $[Fe(Asc)_2]^{-}$ and four coordination compounds Fe(II)-$[Fe(HAsc)]^{+}$; $[Fe^{II}Fe^{III}(HAsc)_2(OH)_2]^{+}[Fe(HAsc)_2]^{0}$; $[Fe(Asc)]^{0}$. Models of ionic equilibria have been compiled, and the domination areas of the complexes have been determined.

Introduction

Ascorbic acid is a rare polyfunctional compound. It can oxidize and regenerate. It participates in the basic energy processes of plant cells, i.e., in photosynthesis [1, 87-88]. The participation of this acid in the processes of growth, reproduction, vegetative and enzymatic differentiation, water metabolism, enzyme activity [2, 32], and development (stimulation) of metabolic reactions in connection with nucleic acid metabolism and synthesis is very important [3, 40-42, 4, 36]. For biotechnology, special attention is paid to the accumulation of ascorbic acid in crops for plant tissues and accelerating their growth by ascorbate.

Ascorbic acid and its derivatives are used in medicine as antiviral and anticancer drugs and have received much attention. Vitamin C has been defined as the bilateral conversion of the reduced and oxidized forms of ascorbic acid [5, 19-20]. However, dehydroascorbic acid is not always converted to ascorbic acid, although the breakage of the lactone chain leads to the irreversible formation of dicetogulogolic acid. A comprehensive study of the entire ascorbic acid system in plant metabolism, considering organic acids and the enzymatic system of ascorbic acid oxidation and reduction, is necessary to assess the importance of ascorbic acid [6, 55-55]. 56].

Ascorbic acid is an organic compound essential for humans and serves to stabilize the function of connective tissues and bones.
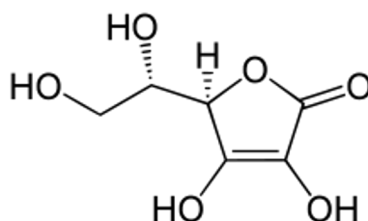
The work aims to study the complexation processes in the Fe(II)-Fe(III)-H$_2$Asc-H$_2$O system at 298.16 K and a solution ionic strength of 0.5 mol/L, using the oxidation potential.

Experimental techniques

Iron (II) and (III) sulfate salts were used in the experiments. The concentration of divalent iron was determined by the bichromatometric method in the presence of a diphenylamine indicator. The amount of ascorbic acid was determined by weighing [7, 225-226, 8, 383-394, 9, 126-137].

The concentration of Fe(III) was determined by the trilonometric method in the presence of an acetate buffer indicator [10, 383-386]. The concentration of sodium hydroxide was determined by direct titration with 0.1 M HCl solution. The composition of the coordination compounds formed in solution is affected by the concentration of ligands and complexing metals, the pH of the solution, the ionic strength, and temperature [7, 225-226]. A constant ionic strength in solution must be obtained by adding an indifferent electrolyte whose ions do not form bonds with the starting substance, such as sodium nitrate.

EMF is determined by potentiometry in an electrolytic cell with platinum, glass, and silver chloride electrodes, an inert gas tube, and a microburette.

The EMF is measured using two galvanic cells:

Pt test solution||KCl (sat.), AgCl | Ag (I)

Ag| AgCl, (HCl 0.1N)| glass | test solution|| KCl (sat.), AgCl|Ag (II)

The first galvanic element is used to measure the system's EMF, and the second to determine the pH of the solution. To prevent the oxidation of divalent iron, a saturated inert gas is continuously passed through the working solution. EMF is measured using a pH-meter-150MP [8, 383-394].

The first working solution contains an equimolecular mixture of salts (nitrates, perchlorates) of Fe(III) and Fe(II). The divalent and trivalent iron concentration must be in the range $1*10^{-4} \div 1*10^{-2}$, and the acid must be from $1*10^{-1}$ to $1*10^{-2}$ mol/L [10, 383-386]. For constancy of the ionic strength of the first working solution, nitric (hypochloric) acid is used. The second working solution differs only because the ionic strength is maintained at a constant value with sodium nitrate (perchlorate) and sodium hydroxide. When the first working solution is titrated with the second, the pH shifts to an alkaline medium [11, 12-19, 12, 123 -138].

According to the experimental dependence of the system EMF on the concentration index of Fe(III) ions (pCFe(III)), numerical values of the slope angle of the curve are obtained, and the nucleus of the Fe(III) complexes formed, and then similarly Fe(II) and HL are determined.
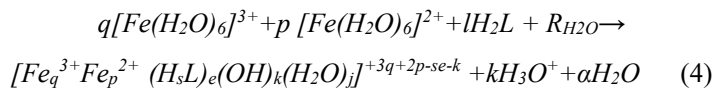
According to the theory of the oxidation potential method [13, 17-28, 14, 78-83, 15, 67-71, 16, 9-19], the complex reaction of iron (II) and iron (III) in all forms of ascorbic acid during hydrolysis [17, 21-29] is expressed by the following equations

$q[Fe(H_2O)_6]^{3+} + xH_2L + kH_2O \rightarrow [Fe_q(M_sL)_x(OH)_y(H_2O)i]^{m+} + yH_3O^+ + jH_2O$ (1)

$p[Fe(H_2O)_6]^{2+} + lH_2L + kH_2O \rightarrow [Fe_p(H_sL)_e(OH)_\vartheta(H_2O)j]^{n+} + \vartheta H_3O^+ + jH_2O$ (2)

where: q and p are the nuclei of iron (III), and iron (II) complexes, l, x are the number of ligands (L-), i, j are the coordinated number of water molecules, ϑ is the coordinated number of HA groups, s is the number of protons in the complex. m, n, are related by the following equation

$$i=6q-sx-y; \quad m=3q-sx-y; \quad j=6p-ls-\vartheta; \quad n=2p-2ls-\vartheta \quad (3)$$

As a result of the formation of heterovalent compounds in the system under study, the following reaction is possible:

$$q[Fe(H_2O)_6]^{3+}+p\,[Fe(H_2O)_6]^{2+}+lH_2L + R_{H2O}\rightarrow$$

$$[Fe_q^{3+}Fe_p^{2+}\,(H_sL)_e(OH)_k(H_2O)_j]^{+3q+2p-se-k} +kH_3O^+ +\alpha H_2O \quad (4)$$

Taking into account equations (1, 2) to express the equilibrium ionic constant, the electromotive force for the galvanic cell is defined as follows:

$$E = E^0 + \frac{\nu}{2}lgC_0 + \frac{\nu}{2}lg\sum_1^q\sum_0^s\sum_0^l\sum_0^k q\beta_{qslk}^{\frac{1}{q}}G_{qslk}^{\frac{q-1}{q}}[H_sL^{n-}]^{\frac{1}{q}}h^{-\frac{k}{q}}$$

$$(5)$$

where G_{qrsek} is the equilibrium concentration of the complex compound; β_{qrsek} is the total constant of formation of these bonds; h is the activity of hydrogen ions.

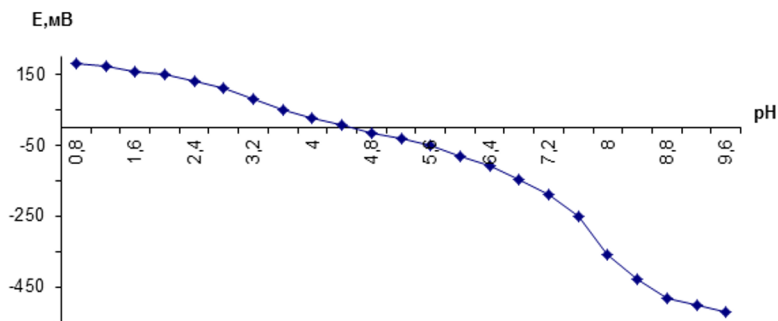First, the experimental curves of dependence of ECF (E, mV) on (pH) were determined (Fig. 1).

FIG. 1. Dependence of electromotive force of system Fe(II)-Fe(III)-HAsc-H$_2$O (E, mV) on pH at 298.16 K; CFe(II) = CFe(III) = $1*10^{-3}$; At H$_2$Ask = $1*10^{-2}$; J = 0.5 mol/L.

According to the Nernst's equation, the decrease in the system EMF with increasing pH in the acidic medium indicates the formation of Fe(III) complexes. The complex formation process occurs in a wide pH range from 0.8 to 9.6. Further, hydrolysis of iron begins, and a brown precipitate appears. To determine the exact composition of the resulting coordination compounds, it is necessary to obtain experimental curves of dependence of EMF on pCo; pCr; pCL.

All the experimental curves necessary to determine the composition of the complexes were obtained under the above conditions. Such dependences were obtained at 298.16 K. The experimental values of the angular coefficients of dependences of EMF from all concentration variables of the Fe(II)-Fe(III)-HAsc-H$_2$O system are given in Table 1. The compositions of the complexes formed in the system were determined from the slopes of the curves. From the numerical

values of the slopes of the obtained curves (Table 1), the stoichiometric matrix allows to develop a chemical model of the equilibria of the system (Tables 2 and 3)

TABLE 1. Experimental values of angular coefficients of EMF dependences on concentration variables of the Fe(II)-Fe(III)-Has-c-H_2O system;

$C_{Fe(II)} = C_{Fe(III)} = 1 \cdot 10^{-3}$; $C_{H2Ask} = 1 \cdot 10^{-2}$; J=0.5 mol/l, T=298,16 K.

№	Dependence of system EMF on concentration parameters				Composition of complexes
	pH	pC_o	pC_r	pC_L	
1	-ν	-ν	0	ν	[FeHAsc]$^{3+}$
2	-2ν	-ν	0	2ν	[Fe(Ask)$_2$]$^-$
3	-ν	0	ν	ν	[FeHAsc]$^+$
4	-ν	0	ν	ν	[FeHAsc]^0
5	-2ν	0	2ν	2ν	[Fe(HAsk)$_2$]^0
6	-2ν	-ν	ν	2ν	[Fe^{II}Fe^{III}(HAsk)$_2$]$^{3+}$
7	-2ν	-ν	ν	2ν	[Fe^{II}Fe^{III}(HAsk)$_2$(OH)$_2$]$^+$

Considering the numerical values of the slopes of the experimental curves and the first derivatives of the EMF from one of the concentration variables when all other variables are constant, a chemical model of the equilibria of the studied system is made (Tables 2 and 3).

TABLE 2.

Chemical model of formation of coordination compounds of Fe(III) with ascorbic acid at 298.16 K, ionic strength of solution I = 0.5;

$C_{Fe(III)} = C_{Fe(II)} = 1 \cdot 10^{-3}$ ва $C_L = 1 \cdot 10^{-2}$ mol/L

Fe(III)	Fe(II)	H	L	OH	Composition of complexes
q	p	s	l	k	
1	0	1	1	0	[Fe(HAsc)]$^{2+}$
1	0	0	1	0	[Fe(HAsc)]$^+$
1	1	2	2	2	[Fe^{II}Fe^{III}(HAsc)$_2$(OH)$_2$]$^+$
1	0	0	1	0	[FeAsc]$^+$
1	0	0	2	0	[Fe(Asc)$_2$]$^-$

The table below shows that Fe(III) forms 5 coordination compounds of different composition: [Fe(Hasc)]$^{2+}$; [Fe(Hasc)]$^+$; [FeIIFeIII(Hasc)$_2$(OH)$_2$]$^+$; [FeAsc]$^+$; [Fe(HAsc)$_2$]$^-$. One heterovalent complex contains two hydroxyl [18, 13-19] groups and two HAsc$^-$ anions in the inner coordination sphere.

Fe(III)	Fe(II)	H	L	OH	Composition of complexes

q	p	s	l	k	
0	1	1	1	0	$[Fe(HAsc)]^+$
0	1	1	2	0	$[Fe(HAsc)_2]^0$
1	1	2	2	2	$[Fe^{II}Fe^{III}(HAsc)_2(OH)_2]^+$
0	1	0	1	0	$[Fe(Asc)]^0$

TABLE 3.

Chemical model of formation of coordination compounds of Fe(II) with ascorbic acid at 298.16 K, ionic strength of solution I = 0.5;

$C_{Fe(III)} = C_{Fe(II)} = 1 \cdot 10^{-3}$ ва $C_L = 1 \cdot 10^{-2}$ mol/L

Chemical models (Tables 2 and 3) are compiled for the complex compounds of the general composition $Fe^{III}_q Fe^{II}_p H_s Ask_l (OH)_k$ [19, 229-231, 20, 87-94].

Tables 4 and 5 show the expressions of the electromotive forces of the system that correspond to each of the formed Fe(III) and Fe(II) coordination compounds, respectively.

TABLE 4. Electromotive force expression of galvanic cell system Fe(II)-Fe(III)-H$_2$Asc-H$_2$O for iron (III) coordination compounds;

$C_{Fe(II)} = 1 \cdot 10^{-3}$; C $_{H2Ask} = 1 \cdot 10^{-2}$ I=0.5 mol/L

№	Composition of complexes	Electromotive force expression of galvanic cell
1	$[Fe(HAsc)]^+$	$E = E° - vlg\beta_{10110} \cdot Ca \cdot K_{a_1} \cdot h^{-1}$
2	$[Fe(HAsc)_2]^0$	$E = E° - vlg\beta_{10110} \cdot Ca \cdot K_{a_1} \cdot h^{-1}$
3	$[Fe^{II}Fe^{III}(HAsc)_2(OH)_2]^+$	$E = E° - vlg\beta_{11222} \cdot K_{a_1}^2 Ca^2 \cdot h^{-6}[Fe^{3+}]$
4	$[Fe(Asc)]^0$	$E = E° - vlg\beta_{10010} \cdot Ca^2 \cdot K_{a_1}^2 K_{a_2}^2 \cdot h^{-2}$
5	$[Fe(Asc)_2]^-$	$E = E° - vlg\beta_{10020} \cdot Ca^2 \cdot K_{a_1}^2 K_{a_2}^2 \cdot h^{-4}$

TABLE 5. Electromotive force expression of galvanic cell system Fe(II)-Fe(III)-H$_2$Asc-H$_2$O for iron (II) coordination compounds;

$C_{Fe(II)} = 1 \cdot 10^{-3}$; C $_{H2Ask} = 1 \cdot 10^{-2}$ I=0.5 mol/L

№	Composition of complexes	Electromotive force expression of galvanic cell
1	$[Fe(HAsc)]^{2+}$	$E = E° - vlg\beta_{01110} \cdot Ca \cdot K_{a_1} \cdot h^{-1}$
2	$[Fe(HAsc)]^+$	$E = E° - vlg\beta_{01120} \cdot Ca^2 \cdot K_{a_1}^2 K_{a_2}^2 \cdot h^{-2}$

3	$[Fe^{II}Fe^{III}(HAsc)_2(OH)_2]^+$	$E = E^\circ - vlg\beta_{11222} \cdot K_{a_1}^2 Ca^2 \cdot h^{-6}[Fe^{3+}]$
4	$[FeAsc]^+$	$E = E^\circ - vlg\beta_{01010} \cdot Ca^2 \cdot K_{a_1}^2 K_{a_2}^2 \cdot h^{-2}$

References

[1] Bohinski R. Modern views in biochemistry / R. Bohinski // -M., 1987. - 543 c.

[2] Zemlyanukhin A.A. Physiological role of ascorbic acid and tricarboxylic acids in plants / A. A. Zemlyanukhin // Diss. D. in Biology. -Voronezh, 1964. - 501 c.

[3] Söding G. Plant growth substances / G. Söding // -M., 1955. - 388 c.

[4] Dobrynina, N.A. Bioorganic chemistry / N.A. Dobrynina, O.T. Zinina. - MOSCOW STATE UNIVERSITY, 2007. - 36 c.

[5] Spiridonova N.S. Ascorbic acid in plants / N.S. Spiridonova // Sverdlovsk: Middle Urals Book Publishers, 1968. - 80 c.

[6] Poling L. Vitamin C and health / L. Poling // -M., 1974. - 80 c.

[7] Charlo G. Methods of Analytical Chemistry. Quantitative analysis of inorganic compounds /Translated from French Yu.Y. Lurie. -M.: Chemistry, 1965. -930 c.

[8] Robinson R., Stokes R. Solutions of electrolytes, 1963. - C.383-394.

[9] Harned G., Owen B. Physical chemistry of electrolyte solutions, 1952. - 558c.

[10] Przybyl, R. Komplexons in chemical analysis / R. Przybyl transl. from Czech under the editorship of Yu. - YU.YU. LUR'YE. - C. 383 - 386.

[11] Suslennikova V.M. Guide for preparation of titrated solutions / V.M. Suslennikova, E.K. Kiseleva. - L. : Chemistry, 1968. - 45 - 71 c.

[12] Korostelev, P.P. Preparation of Solutions for Chemical Analytical Works / P.P. Korostelev .-M. : USSR Academy of Sciences, 1962. -311c.

[13] Eshova G.B. Oxredmetric determination of composition and stability of coordination compounds in homogeneous systems / G.B. Eshova, M. Rakhimova, J.A. Davlatshoeva, M.B. Jorobekova / TSTU, - Dushanbe: 2021. 72 c.

[14] Nikolsky B.P. Oxredmetry / B.P. Nikolsky, V.V. Palchevsky, A.A. Pendin, H.M. Yakubov // -L.: Chemistry. -1975. -305 c.

[15] Zakharevsky M.S. Oxredmetry. - L: Chemistry. -1967.-118c.

[16] Yakubov H.M. Application of oxredmetry to the study of complex-formation. -Dushanbe: Donish. -1966. -121 c.

[17] Nikolsky, B.P. Brief reports on the application of the method of oxidative potential to the study of complex formation in aqueous solutions / B.P. Nikolsky, V.V. Palchevsky, H.M. Yakubov // Chemistry and thermodynamics of solutions. -L.: LENINGRAD STATE UNIVERSITY. -1964. -C. 203-243.

[18] Rakhimova M. Faizulloev E.F. Boboev M.U. Ismailova M.A. / Processes of formation of iron hydroxocomplexes in different media // Scientific monograph. Saarbrucken, Germany: academic publishing house "LAPLAMBERT", - 2017. - 145 c.

[19] Mukhammadieva H.A. Complexation in the system Fe(0)-Fe(II)-ascorbic acid-water / H.A. Mukhammadieva, J.A. Davlatshoeva, L.V. Kvyatkovskaya // Proceeding of the International Symposium On Innovative development of science December 10, 2020, Dushanbe, Tajikistan

Research Center of Innovative Technologies Tajikistan National Academy of Sciences. -Dushanbe, 2020. -C 229-231.

[20] Muhammadieva H.A. The study of the complexation processes in the system Fe(0)-Fe(II)-ascorbic acid-water at 298 K / H.A. Muhammadieva, J.A. Davlatshoeva, L.V. Kviatkovskaya, M. Rakhimova // Proceedings of Osh University of Technology, 2/2020. -C. 87-94.