ACTA CHEMICA SCANDINAVICA 21 (1967) 2759–2772

Equilibrium Studies of L-Ascorbate Ions

I. Equilibria between Ascorbate Ions and Protons in 3 M $Na(ClO_4)$ Medium

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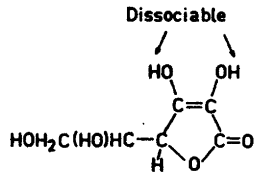
Measurements have been carried out at 25°C as a series of potentiometric titrations, using a glass electrode or a hydrogen electrode. The total concentration of ascorbic acid, C, had values between 0.01 M and 1 M. The values of log $[H^+]$ ranged from -11.5 to -2.0. With $C \leq 0.1$ M essentially only mononuclear species are formed. The data for $C \leq 0.25$ M gave evidence for polynuclear species. The calculated mean composition of the complexes and projection maps indicated the presence of mononuclear and dinuclear complexes. The generalized least squares program LETAGROPVRID was used to test various complex combinations and to refine the final formation constants. These calculations also gave some evidence for $H_5Asc_3^-$. The reactions with their constants and errors, given as 3 σ (σ is the standard deviation), found are:

$HAsc^- + H^+ \rightleftharpoons H_2Asc$	$\log \beta_1 = 4.35_9 \pm 0.006$
$2\ HAsc^- + H^+ \rightleftharpoons H_3Asc_2^-$	$\log \beta_{12} = 4.45 \pm 0.04$
$2\ HAsc^- + 2\ H^+ \rightleftharpoons H_4Asc_2$	$\log \beta_{22} = 8.56 \pm 0.05$
$HAsc^- \rightleftharpoons Asc^{2-} + H^+$	$\log \beta_{\bar{1}1} = -11.34_2 \pm 0.007$

This article is the first in a series of investigations of the solution equilibria of ascorbate ions and bivalent metal ions. It was necessary to start with a study of the acid-base equilibria of ascorbic acid.

The dissociation of ascorbic acid has been studied by a number of earlier investigators (Table 1). The constants given show a large variation, depending partly upon the different experimental circumstances. Ascorbic acid behaves in dilute solutions as a nonassociated dibasic acid H_2Asc. Polynuclear complexes H_pAsc_r do not seem to have been observed before.

The ion $HAsc^-$ predominates in a very broad range of log$[H^+]$. In this paper $HAsc^-$ will be written as C, hence H_2Asc = HC, omitting the charge for simplicity. The structural formula of ascorbic acid may be written:



LIST OF SYMBOLS

C	total concentration of C (2)
c	free concentration of C, $c = [HAsc^-]$ (2)
$\mathbf{C}$	a normalized quantity corresponding to C (9)
C_1	total concentration of mononuclear species $= [H_2Asc] + [HAsc^-] + [Asc^{2-}]$ (5)
E	measured emf in mV (1)
E_{oh}	a constant in $E = E_{oh} - 59.155 \log h + E_j$ (1)
E_j	liquid junction potential (1)
H	excess (analytical) concentration of hydrogen ions over H_2O and $HAsc^-$ (2)
h	free concentration of H^+ (1), (2)
l	$l = \beta_{22}\beta_1^{-1}\beta_{12}^{-1}$ (12)
p	number of H^+ in the complex H_pC_r
$\bar{p}_n$	average number of H per polynuclear complex (5)
r	number of C in complex H_pC_r
$\bar{r}_n$	average number of C per polynuclear complex (5)
$\bar{R}^{-1}$	average degree of condensation of C (4)
U	$U = \sum(Z_{calc}-Z)^2$ or $U = \sum(Z_{calc}-Z+\delta Z)^2$ by introducing δZ
u	a normalized quantity corresponding to h (3), (9)
v	a normalized quantity corresponding to c (9)
w	a normalized quantity corresponding to h (6)
x	a normalized quantity corresponding to h^{-1} (14)
Z	average number of H^+ per C (2)
δZ	systematic error in Z
Z_1	average number of H^+ per C in the mononuclear species (5)
β_{pr}	$\beta_{pr} = [H_pC_r]h^{-p}c^{-r}$; equilibrium constant for the formation of H_pC_r
$\sigma(Z)$	standard deviation in Z as defined in Ref. 16
$\sigma(\beta_{pr})$	standard deviation in β_{pr} as defined in Ref. 16.

EXPERIMENTAL

Chemicals and analysis

Sodium perchlorate was prepared by neutralizing twice recrystallized $NaHCO_3$ (Merck *p.a.*) with perchloric acid (Merck *p.a.*). The neutral solution ($-8 \leq \log h \leq -7$) was allowed to stand for a week to precipitate silicates and heavy metal hydroxides, occurring as small impurities.[17,18] The sodium perchlorate was then recrystallized [19] once, after which no Cl^-, silica, or protolytic impurities could be detected. $NaClO_4$ solutions were

Table 1. Previous pK_a values for ascorbic acid.

Investigator	Method	Medium	Temp. °C	pK_{a1}	pK_{a2}
Karrer, Schwarzenbach and Schöpp [1]	Hydrogen electrode	→ 0	24	4.10	
Birch and Harris [2]	—»—	I = 0.231 M	17.5	4.17	
—»—	—»—	—»—	18		11.57
Kumler and Daniels [3]	—»—	I = 0.0269 M	22—23	4.12	11.51
Ball [4]	—»—	→ 0, KCl	30	4.21	
Carpéni [5]	Hydrogen electrode and glass electrode	Low ionic strength	20	4.25 ± 0.02	11.63
Gal [6]	Glass electrode	→ 0, $NaClO_4$	25	4.20	
Ghosh and Rakshit [7]	Conductivity	Low ionic strength	29	4.20	
—»—	Hydrogen electrode	—»—	29		11.57
Vavrin [8]	Polarography	Phosphate buffers	25	5.92	
Cattaneo and Sartori [9]	—»—	—	25	5.5	
Nebbia and Pizzoli [10]	Optical rotation	—		4.09	11.33
Bell and Robinson [11]	Spectrophotometry	Acetate buffers	25	4.25	
Sobkowska and Minczewski [12]	Electromotive force	1 M $NaClO_4$	20	4.20	
Taqui Khan and Martell [13]	Glass electrode	0.10 M (KNO_3)	0.4	4.49	12.72
Taqui Khan and Martell [13]	—»—	—»—	25	4.04	11.34
Lundgren and Wahlberg [14]	—»—	2 M Na(Cl)	25	4.08	11.09
Wahlberg and Ulmgren [15]	—»—	2 M Na(Cl)	25	4.08 ± 0.02	11.14 ± 0.10

analyzed by evaporating a known volume of the solution at 120°C and drying to a constant weight at the same temperature.

Perchloric acid. Merck *p.a.* was used. The acid was standardized against $KHCO_3$ and Tl_2CO_3. Different determinations agreed within ± 0.1 %.

Sodium hydroxide. A 50 % stock solution was prepared from the EKA Bohus *p.a.* product. From this stock solution portions were taken and diluted with de-aerated water. NaOH solutions were standardized against a previously standardized $HClO_4$-solution. The amount of Na_2CO_3 was less than 0.1 % of the concentration of NaOH.

Silver perchlorate solution. A cation exchanger was saturated with a solution of $AgNO_3$ (Merck *p.a.*) and eluted using a sodium perchlorate solution.

L-*Ascorbic acid*, $C_6H_8O_6$. Using two different preparations, Merck's *p.a.* and Kebo's *puriss.* crystallized, no difference could be detected in the emf titrations. The ascorbic acid was dried over conc. H_2SO_4, but the weight did not change. Determination of the molecular weight by titrations with standardized sodium hydroxide gave exactly the theoretical value (176.1 ± 0.2) g mole^{-1}. The melting point was 189—192°C (v. Euler gives 190—192°C [20]). Powder photographs showed distinct lines. Merck's *p.a.* product, recrystallized in 0.01 M $HClO_4$ and dried in a desiccator, was analyzed with the same result. Ascorbic acid was weighed in for each titration.

Apparatus

Potentiometer. Radiometer's PHM4c, which was calibrated against a Leeds and Northrup potentiometer of type K 3 used together with a Multiflex galvanometer and

a saturated Weston standard cell. The emf values could be read to an accuracy of ± 0.2 mV.

Salt bridge. "The Wilhelm type".[21]

Electrodes. Glass electrode 41260 from Beckman. Hydrogen electrodes prepared according to Bates.[22] Ag,AgCl electrodes according to Brown.[23]

Thermostat. In the measurements we used an oil bath thermostat at 25.00 ± 0.05°C placed in a room at 25.0 ± 0.5°C.

The equilibrium solution was stirred by a stream of N_2-gas. Traces of oxygen had been removed by passing the gas through a column of activated copper at 180°C.[24] The gas was then washed in three bottles containing 10 % H_2SO_4, 10 % NaOH, and 3 M $NaClO_4$.

THE EMF MEASUREMENTS

In our measurements we have used the constant ionic medium, 3 M $Na(ClO_4)$, to keep the activity factors constant. Studying anions, we have chosen $[Na^+] = 3$ M. The emf's of the following cells were measured:

$$-\text{glass electrode} \,/\, S \,/\, RE +$$
$$-\ Pt,\ H_2\ (1\ atm) \,/\, S \,/\, RE +$$

where the reference electrode RE = 3 M $NaClO_4$/0.010 M $AgClO_4$, 2.990 M $NaClO_4$/AgCl,Ag. The equilibrium solution S contained C M $[H_2Asc]_{tot}$, 3 M $Na(ClO_4)$ and had the excess (analytical) hydrogen ion concentration $= H$ M.

H in S was varied by adding from a buret a solution T to the equilibrium solution S. T had the same $[H_2Asc]_{tot}$ and $[NaClO_4]$ as S, but a different H value (usually lower).

Assuming the activity factors to be constant the following expression holds

$$E = E_{oh} - 59.155 \log h + E_j \qquad (1)$$

In each titration E_{oh} and E_j were obtained by a graphical method [19] in the most acidic part, $0.020 \leq h \leq 0.150$ M, where the dissociation of ascorbic acid can be neglected. For the liquid junction potential we have found $E_j = j \cdot H$, where $j = (17 \pm 1)$ mV/M [19,25,31] valid for all C values. E_{oh} is a constant within each titration with constant C. A special titration was performed in order to study the variation of E_{oh} with C. C was varied and h was kept constant at 0.050 M. We obtained: $E_{oh} =$ const. $- 13C$, where E_{oh} is in mV and C in M (see Fig. 1). Similar observations have previously been made for boric acid [19]

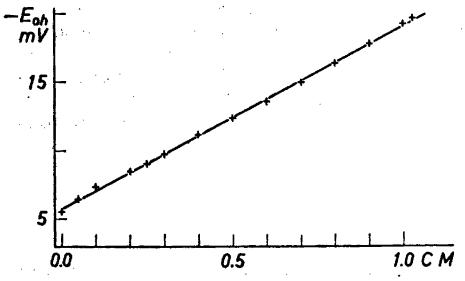


Fig. 1. E_{oh} as a function of the total ascorbic acid concentration C at $h = 0.050$ M.

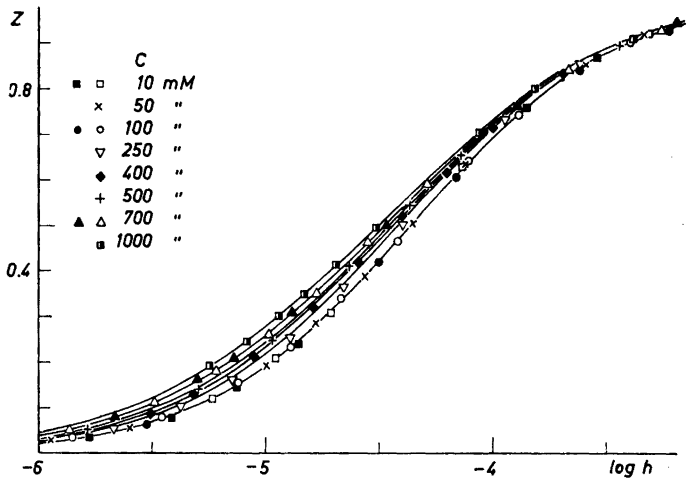


Fig. 2. Z = the average number of H^+ bound to one $HAsc^-$ as a function of log h. The curves have been calculated with the final values of the formation constants using HALTAFALL.* Filled symbols represent hydrogen electrode titrations. Open and half filled symbols represent glass electrode titrations. The symbols ●, ◆, and ▲ represent back titrations.

* HALTAFALL[37] is a recent version of HALTA[16] worked out by L. G. Sillén and N. Ingri.

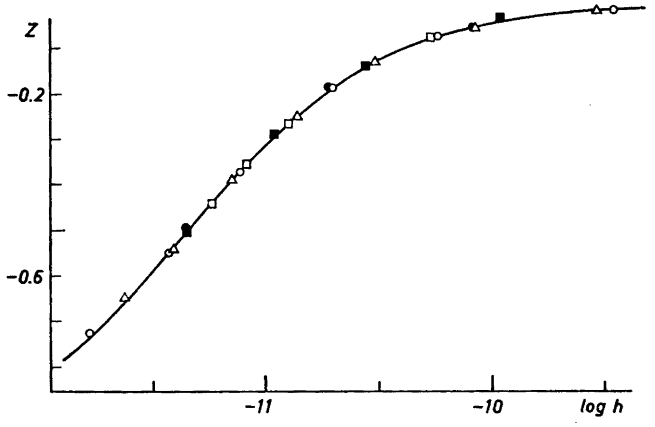


Fig. 3. Z = the average number of H^+ bound to one $HAsc^-$ as a function of log h. The curve is the normalized function $-[x/(1+x)](\log x)$ in the position $\log x - \log h = \log \beta_{\bar{1}1} = -11.34$. Filled symbols represent back titrations made with hydrogen electrodes. Open symbols represent forward titrations made with glass electrodes. (□ C=10 mM; △ C=50 mM; ○ C=100 mM.)

and acetic acid.[26,27] The variation of E_{oh} with C could not be described by the formation of an acid complex H_3Asc^+, but may be due to a variation of the activity factors with the ionic medium. Using a Gran-diagram [28] a check of H in the buret solution and starting equilibrium solution was obtained.

After an addition from the buret the emf values became constant 5 to 10 min later using a glass electrode, and 10 to 20 min later using a hydrogen electrode. The emf kept a constant value for at least 12 h.

Back titrations show that the equilibria are reversible. Glass electrode titrations were checked by hydrogen electrode titrations. The agreement was excellent, even in the alkaline range where some points have been taken at such low log h values as -11.0 to -11.5. The reproducibility is very good (see Figs. 2 and 3).

SURVEY OF EXPERIMENTAL DATA

From the emf measurements we get $[H^+] = h$ (eqn. (1)). From the analysis we know H and C. The data C, H, h have been transformed to $Z(\log h)_C$ using eqn. 2a. (Figs. 2 and 3, Table 2). Z_{calc} in Table 2 was obtained from the general relationships in 2b:

$$CZ = H - h + K_w h^{-1} \quad (2a); \quad CZ = \sum p\beta_{pr} h^p c^r; \quad C = \sum r\beta_{pr} h^p c^r \quad (2b)$$

For the ionic product of water in 3 M $NaClO_4$ we have used the value log $K_w = -14.22 \pm 0.01$.[19,29]

Table 2. Experimental data.

In the range $-6.5 \leq \log h \leq -2.0$, Z_{calc} has been calculated with log $\beta_1 = 4.359$ for $C \leq 0.1$ M and log $\beta_1 = 4.36$, log $\beta_{12} = 4.45$, log $\beta_{22} = 8.56$ for $C \geq 0.25$ M. In the range $-11.5 \leq \log h \leq -9.0$, Z_{calc} has been calculated with log $\beta_{11}^- = -11.34$. The values of $(Z_{calc} - Z)$ were obtained using LETAGROPVRID.

$Z(\log h)_C$, $-6.5 \leq \log h \leq -2.0$, glass electrode titrations

$C = 0.010$ M. $-\log h$, Z, $10^3(Z_{calc} - Z)$; 3.315, 0.917, 0; 3.395, 0.905, −3; 3.636, 0.842, −1; 3.888, 0.757, −9; 4.133, 0.628, 0; 4.421, 0.461, 4; 4.716, 0.308, −2; 4.960, 0.206, −5; 5.239, 0.121, −4; 5.776, 0.037, 0.

$C = 0.050$ M. $-\log h$, Z, $10^3(Z_{calc} - Z)$; 3.041, 0.956, −2; 3.337, 0.914, −1; 3.591, 0.854, 0; 3.868, 0.757, −1; 4.120, 0.634, 1; 4.350, 0.504, 2; 4.564, 0.386, −2; 4.782, 0.282, −8; 4.997, 0.192, −5; 5.254, 0.119, −6; 5.602, 0.060, −6; 5.947, 0.031, −6; 6.490, 0.013, −6.

$C = 0.100$ M. $-\log h$, Z, $10^3(Z_{calc} - Z)$; 2.789, 0.976, −2; 3.067, 0.958, −7; 3.396, 0.899, 3; 3.651, 0.833, 3; 3.897, 0.740, 4; 4.111, 0.636, 3; 4.421, 0.463, 2; 4.671, 0.339, −11; 4.891, 0.231, −4; 5.119, 0.153, −5; 5.457, 0.078, −4; 5.851, 0.035, −4; 6.671, 0.007, −2.

$C = 0.250$ M. $-\log h$, Z, 10^3 $(Z_{calc} - Z)$; 2.810, 0.975, −2; 3.274, 0.925, 2; 3.624, 0.844, 8; 3.949, 0.726, 9; 4.142, 0.634, 11; 4.400, 0.494, 14; 4.654, 0.357, 16; 4.892, 0.244, 18; 5.144, 0.152, 17; 5.376, 0.095, 14; 5.677, 0.051, 7; 6.018, 0.022, 6; 6.370, 0.011, 2.

$C = 0.500$ M. $-\log h$, Z, $10^3(Z_{calc} - Z)$; 3.073, 0.950, 3; 3.442, 0.893, 5; 3.682, 0.833, 5; 3.895, 0.760, 5; 4.140, 0.654, 4; 4.363, 0.544, 2; 4.629, 0.409, 0; 4.968, 0.245, 10; 5.296, 0.138, 8; 5.531, 0.087, 6; 5.785, 0.051, 4; 6.245, 0.018, 2; 6.419, 0.007, 7.

$C = 0.700$ M. $-\log h$, Z, $10^3(Z_{calc} - Z)$; 2.713, 0.980, −1; 3.263, 0.925, 5;3.670, 0.837, 7; 4.006, 0.718, 6; 4.294, 0.587, 3; 4.549, 0.460, 2; 4.781, 0.347, 3; 4.987, 0.258, 5; 5.217, 0.178, 4; 5.491, 0.108, 3; 5.864, 0.051, 2; 6.329, 0.020, −1; 6.708, 0.010, −2.

$C = 1.000$ M. $-\log h$, Z, $10^3(Z_{calc} - Z)$; 2.365, 0.996, −5; 2.715, 0.979, 0; 3.080, 0.953, 0; 3.386, 0.907, 4; 3.597, 0.860, 6; 3.821, 0.793, 6; 4.064, 0.702, 3; 4.304, 0.597, −2; 4.519, 0.494, −4; 4.693, 0.411, −4; 4.836, 0.346, −3; 4.943, 0.299, −1; 5.083, 0.244, 1; 5.242, 0.190, 2.

$Z(\log h)_C$, $-6.5 \leq \log h \leq -2.0$, hydrogen electrode titrations
$C = 0.010$ M. $-\log h$, Z, $10^3(Z_{calc}-Z)$; 3.335, 0.914, 0; 3.545, 0.866, 1; 3.854, 0.757, 5; 4.855, 0.238, 4; 5.124, 0.143, 4; 5.413, 0.078, 3; 5.780, 0.034, 3.
$C = 0.100$ M. $-\log h$, Z, $10^3(Z_{calc}-Z)$; 2.869, 0.966, 3; 3.224, 0.926, 6; 3.618, 0.836, 11; 3.868, 0.747, 9; 4.167, 0.604, 5; 4.505, 0.417, 0; 4.960, 0.194, 7; 5.526, 0.064, 0.
$C = 0.400$ M. $-\log h$, Z, $10^3(Z_{calc}-Z)$; 3.014, 0.958, 1; 3.689, 0.829, 6; 4.005, 0.712, 4; 4.208, 0.613, 7; 4.400, 0.515, 5; 4.591, 0.414, 6; 4.789, 0.315, 8; 5.051, 0.207, 8; 5.313, 0.125, 9; 5.504, 0.083, 10.
$C = 0.700$ M. $-\log h$, Z, $10^3(Z_{calc}-Z)$; 3.195, 0.941, −1; 3.619, 0.848, 10; 3.897, 0.759, 9; 4.131, 0.669, −1; 4.300, 0.582, 5; 4.471, 0.497, 4; 4.628, 0.920, 3; 4.885, 0.306, −2; 5.142, 0.207, −1; 5.303, 0.158, −1; 5.667, 0.078, 1.

$Z(\log h)_C$, $-11.5 \leq \log h \leq -9.0$, $C \leq 0.1$ M, glass electrode titrations
$C = 0.010$ M. $-\log h$, Z, $10^3(Z_{calc}-Z)$; 10.268, −0.079, 1; 10.711, −0.189, 0; 10.895, −0.265, 2; 11.079, −0.354, 1; 11.237, −0.442, 2.
$C = 0.050$ M. $-\log h$, Z, $10^3(Z_{calc}-Z)$; 9.539, −0.016, 1; 10.077, −0.054, 3; 10.523, −0.131, −1; 10.860, −0.249, 1; 11.147, −0.390, 1; 11.405, −0.542, 6; 11.619, −0.647, −7.
$C = 0.100$ M. $-\log h$, Z, $10^3(Z_{calc}-Z)$; 9.467, −0.017, 4; 10.243, −0.076, 2; 10.702, −0.189, 3; 11.111, −0.374, 4; 11.421, −0.551, 6; 11.776, −0.725, −6.

$Z(\log h)_C$, $-11.5 \leq \log h \leq -9.0$, $C \leq 0.1$ M, hydrogen electrode titrations
$C = 0.010$ M. $-\log h$, Z, $10^3(Z_{calc}-Z)$; 9.965, −0.034, −6; 10.560, −0.139, −3; 10.956, −0.288, −3; 11.343, −0.505, 5.
$C = 0.100$ M. $-\log h$, Z, $10^3(Z_{calc}-Z)$; 10.084, −0.055, 3; 10.721, −0.186, −7; 11.350, −0.495, −9.

$Z(\log h)_C$, $-11.5 \leq \log h \leq -9.0$, $C \geq 0.25$ M, glass electrode titrations
$C = 0.250$ M. $-\log h$, Z; 9.036, −0.003; 9.485, −0.012; 9.986, −0.039; 10.317, −0.082; 10.533, −0.127; 10.743, −0.193; 10.922, −0.268.
$C = 0.500$ M. $-\log h$, Z; 9.768, −0.024; 10.303, −0.072; 10.576, −0.124; 10.792, −0.183; 10.975, −0.253; 11.154, −0.332.
$C = 0.700$ M. $-\log h$, Z; 9.528, −0.010; 10.060, −0.037; 10.530, −0.112; 10.833, −0.187; 11.032, −0.262; 11.211, −0.357.

$Z(\log h)_C$, $-11.5 \leq \log h \leq -9.0$, $C \geq 0.25$ M, a hydrogen electrode titration
$C = 0.400$ M. $-\log h$, Z; 9.788, −0.023; 10.572, −0.134; 10.895, −0.232; 11.137, −0.332; 11.470, −0.501.

A special titration, using a glass electrode. Data $E_{oh}(C)_h$
$h = 0.050$ M. C M, $-E_{oh}$ mV: 0.000, 5.5; 0.051, 6.4; 0.100, 7.3; 0.200, 8.4; 0.251, 9.0; 0.300, 9.7; 0.401, 11.1; 0.501, 12.3; 0.601, 13.5; 0.701, 14.9; 0.800, 16.3; 0.900, 17.7; 1.000, 19.2; 1.027, 19.6.

TREATMENT OF THE EXPERIMENTAL DATA IN THE RANGE $-6.5 \leq \log h \leq -2.0$

With $C \leq 0.1$ M the same curve $Z(\log h)_C$ is obtained for different C values (see Fig. 2). The shape of the curve is the same as for a monobasic acid. The best fit with the normalized function [31]

$$[u/(1+u)](\log h);\ u = \beta_1 h \text{ gave } \log \beta_1 = 4.36 \pm 0.02 \qquad (3)$$

Different $Z(\log h)_C$ curves for different C were obtained with $C \geq 0.25$ M. This indicates that polynuclear species are present.

Mean composition of the complexes

We have used a method, worked out by L. G. Sillén,[30] (cf. Rossotti-Rossotti's textbook [31]).

Mean values of p and r were calculated using graphical integration [19] or the computer program MESAK [32] prepared by N. Ingri and L. G. Sillén.

Table 3. Values for $\bar{r}_\pi$ and $\bar{p}_\pi$.

MESAK calculation			graphical calculation		
$-\log h$ $C = 0.500$ M	$\bar{p}_\pi$	$\bar{r}_\pi$	$-\log h$	$\bar{p}_\pi$	$\bar{r}_\pi$
3.40	1.9	2.1	4.20	2.6	2.0
3.79	1.8	2.1	4.40	2.0	2.0
4.04	1.7	2.1	4.60	1.4	2.0
4.25	1.5	2.1	4.80	1.3	2.0
4.45	1.5	2.1	5.00	1.0	2.1
4.65	1.4	2.1	5.20	0.9	2.2
4.84	1.2	2.0	5.40	0.8	2.2
5.09	1.2	2.0			
5.25	1.2	2.0			
5.46	1.2	2.0			
$C = 0.700$ M					
3.79	1.6	1.9	4.20	2.5	1.8
4.05	1.5	1.9	4.40	1.9	1.8
4.27	1.4	1.8	4.60	1.5	1.8
4.47	1.3	1.8	4.80	1.1	1.9
4.67	1.3	1.8	5.00	0.9	2.0
4.89	1.3	1.8	5.20	0.8	2.1

The average degree of condensation of C, R^{-1}, and the free concentration, c, may be calculated from

$$R = R_0 + \int_{Z_0}^{Z} \left(\frac{\mathrm{d}\ln h}{\mathrm{d}\ln C}\right)_Z \mathrm{d}Z \text{ at constant } C \tag{4a}$$

$$\ln c = \ln c_0 + (R - R_0) - \int_{h_0}^{h} Z\ \mathrm{d}\ln h \text{ at constant } C \tag{4b}$$

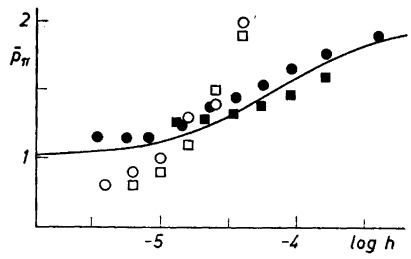


Fig. 4. $\bar{p}_\pi$ = the average number of H^+ bound in each polynuclear complex as a function of log h. The curve is the normalized function $[(1 + 2\omega)/(1 + \omega)](\log \omega)$. Filled symbols represent values calculated by MESAK.[32] Open symbols represent values calculated by graphical integration.[19]

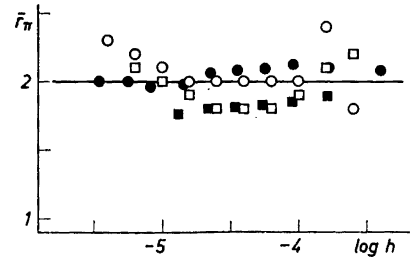


Fig. 5. $\bar{r}_\pi$ = the average number of $HAsc^-$ bound in each polynuclear complex as a function of log h. Filled symbols represent the values calculated by MESAK. Open symbols represent the graphical integration.

The average value of p and r for the polynuclear species, $\bar{p}_\pi$ and $\bar{r}_\pi$, are obtained by:

$$\bar{p}_\pi = (CZ - C_1Z_1)/(CR - C_1); \quad C_1 = c + \beta_1 ch \qquad (5)$$
$$\bar{r}_\pi = (C - C_1)/(CR - C_1); \quad C_1Z_1 = \beta_1 ch$$

The calculated values of $\bar{p}_\pi$ and $\bar{r}_\pi$ are presented in Table 3 and Figs. 4, 5, and 6. $\bar{p}_\pi$ has values between 1 and 2 while $\bar{r}_\pi = 2.0 \pm 0.3$.

This indicates that the predominating polynuclear species are dinuclear with two H^+ attached at $\log h = -2$ and one at $\log h = -5$. If HC_2^- and H_2C_2 were the only polynuclear complexes formed $\bar{p}_\pi = ([HC_2^-] + 2[H_2C_2])/([HC_2^-] + [H_2C_2])$. $\bar{p}_\pi(\log h)$ then should have the same shape as the normalized curve

$$[(1 + 2w)/(1 + w)]\ (\log w);\ w = \beta_{22}\beta_{12}^{-1}h \qquad (6)$$

In Fig. 4 is shown the fit for $\log w - \log h = \log \beta_{22} - \log \beta_{12} = 4.10$, which is as good as can be expected within the limits of error. The next step was to test if the combination C^-, HC, HC_2^- and H_2C_2 fits with the experimental data $Z(\log h)_C$.

Projection maps

If HC, HC_2^-, H_2C_2 are formed the following equations are valid

$$C = c + \beta_1 hc + 2\ \beta_{12}hc^2 + 2\ \beta_{22}h^2c^2 \qquad (7)$$
$$CZ = \beta_1 hc + \beta_{12}hc^2 + 2\beta_{22}h^2c^2 \qquad (8)$$

with the substitutions $\beta_1 h = u$, $\beta_{12}\beta_1^{-1}c = v$, $C\beta_{12}\beta_1^{-1} = \mathbf{C}$ (9)
we get

$$\mathbf{C} = v + uv + 2uv^2 + 2\ lu^2v^2 \qquad (10)$$
$$\mathbf{C}Z = uv + uv^2 + 2lu^2v^2 \qquad (11)$$

where

$$l = \beta_{22}\beta_1^{-1}\beta_{12}^{-1} \qquad (12)$$

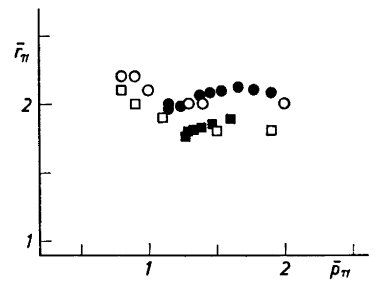


Fig. 6. $\bar{r}_\pi$ *versus* $\bar{p}_\pi$. Filled symbols represent the values calculated by MESAK. Open symbols represent the graphical integration.

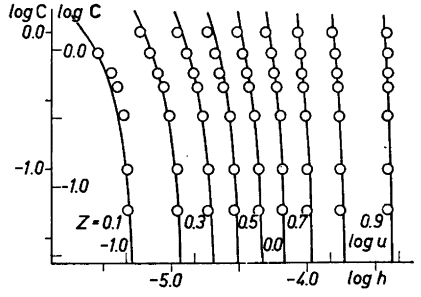


Fig. 7. Projection maps. Experimental data $\log C(\log h)_Z$, represented by the symbols ○ and normalized curves $\log \mathbf{C}(\log u)_Z$ calculated with $\log \beta_1 = 4.36$, $\log \beta_{12} = 4.46$ and $\log \beta_{22} = 8.57$.

From eqns. (10) and (11) log C as a function of log u and Z was calculated.[31] Choosing different values of l, projection maps with curves of different shapes were obtained.

In Fig. 7 is shown the very good agreement between the two projection maps, the theoretical log **C** $(\log u)_Z$ and the experimental log C $(\log h)_Z$. The best fit was obtained with $l = 0.5$ hence $\log l = \log \beta_{22} - \log \beta_1 - \log \beta_{12} = -0.3$ and the following transformations:

$$\log \mathbf{C} - \log C = \log \beta_{12} - \log \beta_{11} = 0.1$$
$$\log u - \log h = \log \beta_1 = 4.36$$

By using projection maps, the following result was thus obtained:

$$\begin{aligned} \log \beta_1 &= 4.36 \pm 0.05 \\ \log \beta_{12} &= 4.46 \pm 0.10 \\ \log \beta_{22} &= 8.52 \pm 0.10 \end{aligned} \qquad (13)$$

Refinement using LETAGROPVRID[33]

Table 4 gives the result of treating the data by the generalized least squares program LETAGROPVRID.

The combination $HC + HC_2^- + H_2C_2$ gives a good fit with the data (see Tables 2, 4 and Fig. 2). The value of $\log \beta_1 = 4.359 \pm 0.006$ obtained in the mononuclear range of C (51 points with $0.010 \leq C \leq 0.100$) differs a little from the value $\log \beta_1 = 4.342 \pm 0.008$ obtained when all points were used in the calculations (125 points with $0.010 \leq C \leq 1.000$). The difference may, *e.g.*, be due to small analytical errors in H and C or to a slight variation of the activity factors at higher values of C or to the presence of small amounts of another complex. If allowance is made for small analytical errors, δZ, by treating the systematic errors as adjustable parameters, we get lower values of the error square sum $U = \sum(Z_{calc} - Z + \delta Z)^2$ and the standard deviation of Z, $\sigma(Z)$, but still somewhat different values of $\log \beta_1$ (see Table 4). However, within the limits of error, the same values of the dimeric constants were obtained using $\log \beta_1 = 4.360$ or 4.342.

The error square sum $U = \sum(Z_{calc} - Z)^2$ and the standard deviation $\sigma(Z)$ are slightly lowered by introducing $H_2C_3^-$. As seen in Table 4 U and $\sigma(Z)$ are lowered still more if instead allowance is made for small analytical errors, δZ. The lowest values of $U = \sum(Z_{calc} - Z + \delta Z)^2$ and $\sigma(Z)$ are obtained if both $H_2C_3^-$ is introduced and δZ are adjusted at the same time. However, the value of 3σ for $\log \beta_{23}$, is fairly high.

We have also tested C_2^{2-}, H_3C_3, HC_3^{2-} and C_3^{3-} but the "best" values of the corresponding β_{pr} were zero within the limits of error (3σ):

$\beta_{02} \pm 3\sigma = (-1.8 \pm 2.4) \times 10^{-2}$, $\log \beta_{02} < -1.6$; $\beta_{33} \pm 3\sigma = (1.8 \pm 4.0) \times 10^{12}$, $\log \beta_{33} < 12.75$; $\beta_{13} \pm 3\sigma = (-1.7 \pm 0.9) \times 10^4$, $\log \beta_{31} < 4$; $\beta_{03} \pm 3\sigma = (-1.5 \pm 0.6) \times 10^{-1}$, $\log \beta_{03} < -1$.

The values of δZ have been adjusted in the following way: a) The formation constants were refined keeping δZ constant for all titrations used in the calculations. b) The values of σZ were refined, keeping the formation constants at a constant value treating each titration apart. This scheme was repeated until we got a minimum value of U. δZ was given a low starting value, *e.g.* 0.

Table 4. Results of LETAGROPVRID calculations using points with C = 0.010, 0.050, 0.100, 0.250, 0.400, 0.500, 0.700, and 1.000 M. $0 \leq Z \leq 1$ and $-6.5 \leq \log h \leq -2.0$. The "final result" has been underlined. $U = \sum(Z_{calc} - Z + \delta Z)^2$.

Number of points	$U \times 10^3$	(σZ)	$\log(\beta_1 \pm 3\sigma)$	$\log(\beta_{12} \pm 3\sigma)$	$\log(\beta_{22} \pm 3\sigma)$	$\log(\beta_{23} \pm 3\sigma)$	The systematic errors	Notes
17	0.24	0.0039	4.360 ± 0.008	—	—	—	$\delta Z = 0$	C = 0.010 M
17	0.14	0.0029	4.359 ± 0.007	—	—	—	δZ adjusted	
51	1.05	0.0046	4.359 ± 0.006	—	—	—	$\delta Z = 0$	C = 0.010, 0.050, and 0.100 M
51	0.58	0.0034	4.357 ± 0.005	—	—	—	δZ adjusted [a]	
95	2.44	0.0052	4.347 ± 0.008	4.37 ± 0.10	8.48 ± 0.08	—	$\delta Z = 0$	All C-values. Points within $0<C(1-Z)<0.3$ M only, that is not more than 10 % of ClO_4^- have been exchanged.
95	1.11	0.0035	4.342 ± 0.006	4.42 ± 0.07	8.53 ± 0.06	—	δZ adjusted	
95	2.09	0.0048	4.347 ± 0.008	4.22 ± 0.08	8.44 ± 0.09	$\log \beta_{23} < 8.89$	$\delta Z = 0$	
95	0.80	0.0030	4.344 ± 0.005	4.27 ± 0.11	8.47 ± 0.06	8.71 ± 0.19	δZ adjusted	
125	4.72	0.0062	4.360	4.41 ± 0.05	8.48 ± 0.04	—	$\delta Z = 0$ β_1 not	All points $0<C(1-Z)<0.8$ M
125	3.31	0.0052	4.342 ± 0.008	4.45 ± 0.04	8.56 ± 0.05	—	$\delta Z = 0$ varied	
125	1.52	0.0035	4.340 ± 0.006	4.46 ± 0.03	8.58 ± 0.03	—	δZ adjusted [b]	
125	2.65	0.0047	4.344 ± 0.007	4.36 ± 0.07	8.52 ± 0.05	8.64 ± 0.24	$\delta Z = 0$	
125	1.02	0.0029	4.341 ± 0.004	4.36 ± 0.05	8.52 ± 0.02	8.61 ± 0.16	δZ adjusted	

[a] The systematic errors, δZ, obtained: C M, 10^3 ($\delta Z \pm 3\sigma$); 0.010, −2.1 ± 2.5; 0.010, 3.0 ± 3.4; 0.050, 3.6 ± 2.4; 0.100; −4.2 ± 4.1; 0.100, 2.4 ± 3.7;

[b] The systematic errors, δZ, obtained: C M, 10^3 ($\delta Z \pm 3\sigma$); 0.010, 1.8 ± 2.5; 0.010, 8.2 ± 4.3; 0.050, 4.2 ± 1.3; 0.100, −7.2 ± 4.2; 0.100, −0.9 ± 3.4; 0.250, −5.5 ± 3.9; 0.400, −2.3 ± 2.9; 0.500, −2.0 ± 3.3; 0.700, −0.7 ± 2.0; 0.700, 0.6 ± 3.7; 1.000, 1.6 ± 3.2;

The values of δZ (see Table 4) seem quite reasonable with respect to the experimental uncertainty. The errors of analysis, reading emfs, volumes etc. we expect to give an error $\delta Z \approx 0.005$.

The variation of the activity factors could possibly be expected to influence the data with high concentration of ascorbic acid, where a considerable amount of ClO_4^- has been replaced by $HAsc^-$.

Hence we have treated a) all 95 points with less than 10% of ClO_4^- replaced by $HAsc^-$, that is $0 < C(1-Z) < 0.3$ M; b) all 125 measured points, that is $0 < C(1-Z) < 0.8$ M; as seen in Table 4 the same equilibrium constants came out within the limits of error and $\sigma(Z)$ was practically the same for the two sets. This indicates that the variation of the activity factors does not influence the data seriously in the range $-6.5 \leq \log h \leq -2.0$.

TREATMENT OF THE EXPERIMENTAL DATA IN THE RANGE $-11.5 \leq \log h \leq -9.5$.

With $C \leq 0.1$ M the curves $Z(\log h)_C$ coincide for different values of C(see Fig. 3). The best fit with the normalized function [31]

$$-[x/(1+x)]\ (\log x);\ x = \beta_{\bar{1}1} h^{-1} \text{ gave } \log \beta_{\bar{1}1} = -11.34 \pm 0.02 \qquad (14)$$

Refinement using LETAGROPVRID gave $\log \beta_{\bar{1}1} = -11.342 \pm 0.007$ with $\sigma(Z) = 0.0043$ and $\sum(Z_{calc}-Z)^2 = 4.4 \times 10^{-4}$. Treating the systematic errors, δZ, as adjustable parameters we got $\log \beta_{\bar{1}1} \pm 3\ \sigma = 11.343 \pm 0.006$, with $\sigma(Z) = 0.0037$ and $\sum(Z_{calc}-Z)^2 = 3.3 \times 10^{-4}$ and the values of δZ: C M, $10^3(\delta Z \pm 3\sigma)$: 0.010, (1.9 ± 6.9); 0.010, (-1.2 ± 1.4); 0.050, (-0.4 ± 4.5); 0.100, (4.6 ± 11.1); 0.100, (-2.2 ± 5.1); The values of δZ are of the expected magnitude 25 points were used in the calculation.

We also have measured 24 points at higher values of C. $Z(\log h)_C$ for $C = 0.25$, 0.40, 0.50, and 0.70 M differs a little from the mononuclear curve, but in this concentration range between 20 and 40 % of the medium ions ClO_4^- have been exchanged, principally to $HAsc^-$ and Asc^{2-}. We think that the variation of the activity factors here may influence the data seriously and therefore we have restricted ourselves only to consider data with $C \leq 0.1$ M in this range of $\log h$.

FINAL RESULT AND DISCUSSION

As the final result we propose the following reactions and constants valid in 3 M $Na(ClO_4)$ medium and at 25°C.

$HAsc^- + H^+ \rightleftharpoons H_2Asc$	$\log \beta_1 = 4.35_9 \pm 0.006$
$2\ HAsc^- + H^+ \rightleftharpoons H_3Asc_2^-$	$\log \beta_{11} = 4.45 \pm 0.04$
$2\ HAsc^- + 2\ H^+ \rightleftharpoons H_4Asc_2$	$\log \beta_{22} = 8.56 \pm 0.05$
$HAsc^- \rightleftharpoons Asc^{2-} + H^+$	$\log \beta_{\bar{1}1} = -11.34_2 \pm 0.006$

With the present data we could not ascertain the presence of $H_5Asc_3^-$. The fractions of ascorbic acid present in different species are represented in Figs. 8 and 9.

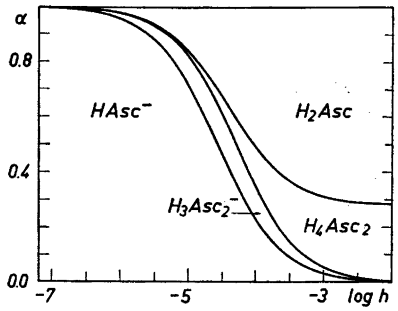


Fig. 8. Distribution diagram for ascorbic acid, calculated using HALTAFALL. $C = 0.4$ M, $-7.0 \leq \log h \leq -2.5$. At a given value of $\log h$ the fraction of ascorbic acid present in H_pAsc_r is represented by the segment of a vertical line falling within the corresponding area.

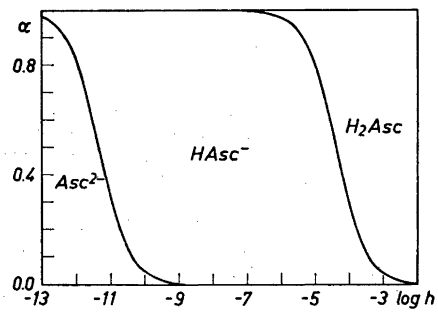


Fig. 9. Distribution diagram for ascorbic acid. $C = 0.01$ M, $-13.0 \leq \log h \leq -2.5$.

Hence, acidic solutions of L-ascorbic acid seem to contain the dimeric species H_4Asc_2 and $H_3Asc_2^-$. Some work to determine the crystal structure of L-ascorbic acid has been done earlier.[34,35] A complete crystal structure has recently been worked out by Dr. Jan Hvoslef in Oslo;[36] he finds that hydrogen bonds are formed from all the five OH groups in the molecule so that infinite units are formed. In the solution one might imagine that the dimers are formed by two H_2Asc forming 2—4 hydrogen bonds with each other; several possible structures may be thought of.

Acknowledgements. The authors want to thank Professor Georg Lundgren who is the initiator of this investigation. We are also indebted to Professor Arne Magnéli and Laborator Peder Kierkegaard for many stimulating discussions. We thank Professor Arne Ölander for his kind interest. In the computing we have in many ways been helped by Professor Lars Gunnar Sillén, which is gratefully acknowledged. Professor Nils Ingri we want to thank for his continuous interest and encouragement. Dr. Björn Warnqvist has given us valuable practical help in the computer work and Mr. Herbert Larsson has given us valuable technical assistance. The English of this paper has been corrected by Dr. George Baldwin.

The experimental work has been carried out in the laboratories of the *Institute of Inorganic and Physical Chemistry, University of Stockholm*, and the automatic computing has been performed at the *Department of Inorganic Chemistry, KTH, Stockholm.*

This investigation was financially supported by a grant from "Anslaget till främjande av ogradueradе forskares verksamhet".

This investigation forms part of a program financially supported by the *Swedish Natural Science Research Council.*

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Received June 27, 1967.