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Equilibrium Studies of L-Ascorbate Ions. IX. Equilibria between Iron(II) Ions, Ascorbate Ions, and Protons in 3 M (Na)ClO$_4$ Medium

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Potentiometric titrations, giving 154 experimental points, have been carried out for the system Fe(II)-ascorbic acid-H$^+$ using glass electrodes. The concentrations ranges studied were 0.01 M$\leq$[Fe^{2+}]$_{\text{tot}}\leq$1 M, 0.02 M$\leq$ [H$_2$Asc]$_{\text{tot}}\leq$0.2 M and $-7.1\leq\log$ [H$^+$] ≤ -1.1, where H$_2$Asc$\equiv$ascorbic acid. Special precautions were taken to keep the system in a reduced state. The following equilibria and equilibrium constants (${}^*\beta_i$) are valid in 3 M (Na)ClO$_4$ and at 25 °C:

$\mathrm{HAsc^- + H^+ \rightleftharpoons H_2Asc}$
$\log\ (\beta_1 \pm 3\sigma) = 4.377 \pm 0.011$

$\mathrm{Fe^{2+} + HAsc^- \rightleftharpoons FeHAsc^+}$
$\log\ (\beta_2 \pm 3\sigma) = 0.21 \pm 0.05$

$\mathrm{Fe^{2+} + HAsc^- \rightleftharpoons FeAsc + H^+}$
$\log\ (\beta_3 \pm 3\sigma) = -6.58 \pm 0.09$

Solutions with log [H$^+$] > -1.0 are green or pale green. When NaOH solution is added the colour turns violet. The experimental data for log[H$^+$] ≥ -5.5 can be explained by the presence of H$_2$Asc, HAsc$^-$, Fe^{2+}, and FeHAsc$^+$ participating in rapid equilibrium reactions. In solutions with log [H$^+$] < -5.5, however, the equilibria are approached slowly. These solutions are black, and seem to contain the species FeAsc, possibly together with polynuclear complexes of the type Fe$_q$Asc$_r$.

The complex formation between Fe(II) and ascorbic acid is of considerable biological interest. For example, the uptake of iron(II) by the human body is more efficient if ascorbic acid is consumed together with iron(II). Ascorbic acid plays an important role in some biochemical processes, where acid-base and redox properties are essential.[1]

We first studied the complex formation between ascorbate and Cd^{2+} and Ca^{2+}, respectively,[2] which are also of biological interest.[1] Violet iron–ascorbate complexes have been reported.[3] Iron(II) is an easily oxidized metal ion, which may take part in redox equilibria with ascorbic acid; this fact necessitates some precautions.

In this paper an equilibrium study of the complex formation between ascorbate and Fe^{2+} is reported. Special care has been taken to keep the system in a reduced state by using H$_2$, H$^+$ as a redox buffer with freshly platinized Pt-foils as a catalyst.

SYMBOLS

The most common symbols are H, B, C for H$^+$, Fe^{2+}, and HAsc$^-$. H = the analytical (excess) concentration of H$^+$ over H$_2$O, Fe^{2+}, and HAsc$^-$. The total concentrations of Fe^{2+} and HAsc$^-$ are written as B and C, respectively. The concentrations of free H$^+$, Fe^{2+}, and HAsc$^-$ are denoted by h, b, and c. The concentration of H$_p$B$_q$C$_r$ is written as c_{pqr}. β_{pqr} is the equilibrium constant for the formation of H$_p$B$_q$C$_r$. The following Z-functions are used:

$Z_{\mathrm{H/C}}$ = the average number of H$^+$ per C, *i.e.* H$^+$ per HAsc$^-$.

$Z_{\mathrm{C/B}}$ = the average number of C per B, *i.e.* HAsc$^-$ per iron(II).

A more complete list of symbols has been given elsewhere.[4]

EXPERIMENTAL

Chemicals and analysis. Solutions of $NaClO_4$, $HClO_4$, NaOH, and NaCl were prepared and analysed as reported earlier.[2,4] Samples of ascorbic acid (*p.a.* from Merck, Darmstadt, Germany) were weighed out for each experiment.

$Fe(ClO_4)_2.6H_2O$ was prepared from the following chemicals: Analysed $FeSO_4.7H_2O$ from I. T. Baker Chemical, Deventer, Holland; Analytical grade $BaCO_3$ and analytical grade $HClO_4$ both from Merck, Darmstadt. First $Ba(ClO_4)_2$ was prepared by neutralizing $HClO_4$ with $BaCO_3$. $FeSO_4.7H_2O$ and $Ba(ClO_4)_2$, respectively, were then recrystallized once from water and mixed in water to give solid $BaSO_4(s)$ and a solution of $Fe(ClO_4)_2$. The amount of Ba^{2+} was adjusted to be slightly in excess ($\sim$0.1 %). A centrifuging with 10 000 rpm was used to separate the solid phase from the solution. The iron(II) perchlorate was recrystallized once. A stock solution made from these crystals was analyzed for Cl^- and SO_4^{2-} by adding $AgNO_3$ and $BaCl_2$ respectively. No precipitation could be detected. The amount of Ba^{2+} was very small (less than 0.1 % of Fe^{2+}). The iron(II) perchlorate solution was treated with hydrogen gas in an acid solution with platinum black as a catalyst. The solution was stored under $CO_2(g)$.

The stock solution of iron(II) perchlorate was analysed by potentiometric titrations with potassium permanganate. The equivalence point was determined by Gran's extrapolation method.[5] The $KMnO_4$-solution (Merck's ampoule) was standardized in two ways: (a) against Merck's *p.a.* As_2O_3 and (b) against 4N8 pure iron wire from Halewood Chemicals Ltd. Different determinations always agreed within 0.1 %.

Apparatus; The salt bridge and electrodes have been described elsewhere.[4]

The titration procedure and emf measurements. For each titration a solution containing iron(II) perchlorate, ascorbic acid, and perchloric acid with $\log h = -1.0$ was prepared and its redox potential decreased by passing a stream of hydrogen gas through it. A freshly platinized platinum foil was used as a catalyst. This

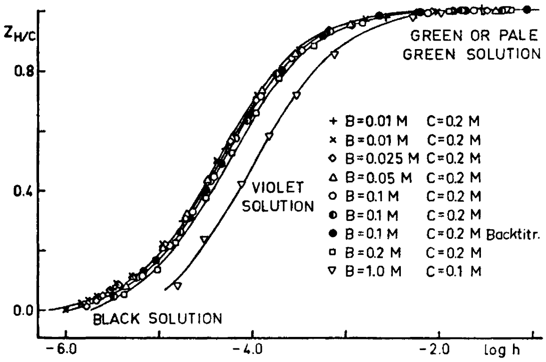

Fig. 1a. $Z_{H/C}$ (= the average number of H^+ bound per C) as a function of log *h*. The curves have been calculated with the final values of the formation constants using HALTAFALL.[11]

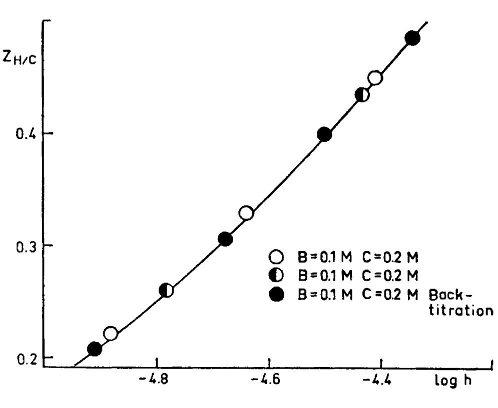

Fig. 1b $Z_{H/C}$ as a function of log *h*. Part of the data in Fig. 1a are shown in a larger scale to demonstrate the reproducibility of the data.

"reduced" solution was used in one buret and a NAOH-solution in the other. Equal volumes from the two burets were added to a solution made from 15.00 ml reduced solution and 15.00 ml distilled and deaerated water (*cf.* Ref. 4). Hydrogen gas was bubbled through the equilibrium solution during the whole titration (in the presence of platinum catalyst). Two glass electrodes, with catalog numbers 39303 and 40495, respectively, from Beckman Instruments, Fullerton, California, were used. For $\log h > -5.5$ (violet solution) the emf became stable within a few minutes, but for $\log h < -5.5$ (black solution) the emf approached a stable value very slowly. However, no precipitate could be detected with a microscope.

We tried to use a hydrogen electrode to measure h in the equilibrium solution. Down to $\log h = -3.5$ there was a very good agreement between glass and hydrogen electrode data, but not for $\log h < -3.5$. The value of E_0 for the hydrogen electrode, however, determined from the most acid points with $0.010\ \mathrm{M} \leq h \leq 0.050\ \mathrm{M}$, was -293 mV, while the expected value is -320 mV (*cf.* Refs. 2 and 6).

The reproducibility of the glass elctrode measurements is within ±0.2 mV. The reversibility of the equilibria was confirmed by one back titration. As seen in Fig. 1b the different titrations agree within ±0.007 in Z.

Table 1a. Experimental data (computer output from LETAGROP). For each point in a titration (≡'Sats') are given V = the volume of the buret solution, with total concentrations H_T, B, and C added to V_0 ml of a solution with total concentrations H_0, B, and C (*cf.* Table 1b); E (≡'E'); $\log [H^+]$ (≡'LOGA'); H (≡'ATOT') and $(H_{calc}-H)10^3$ (≡'DATOT'). H_{calc} has been calculated using the final equilibrium constants. 19 points measured in black solutions with slow equilibria are marked with *.

```
Sats 1  B=0.01M  C=0.02M Vo=30.40ml
    V      EA(MV)    LOGA   ATOT(MM)  DATOT
  0.000   313.70   -1,301    69,62    0,39
  0.800   311.20   -1,344    65,12    0.10
  2.300   306.30   -1,430    57,29   -0,12
  4.300   298.90   -1.557    47,89   -0,22
  6.300   289.80   -1,714    39,52   -0,23
  8.300   277.50   -1,924    32,01   -0,16
 10.300   257.50   -2,264    25,24    0,05
 11.300   238.60   -2,584    22,10    0,18
 13.300   171.40   -3,721    16,25    0,27
 15.300   138.30   -4,281    10,91    0.16
 17.300   111.10   -4,741     6,02   -0,03
 19.300    66.40   -5,500     1,53   -0.14
Sats 2  B=0.01M  C=0.2M  Vo=30.00ml
  0.000   327,60   -1,287   250,91    0,59
  0.820   325.10   -1,331   246,17    0.37
  2.200   321.00   -1,402   238,73    0,70
  4.200   314.10   -1,521   229,01    0,82
  6.400   304,90   -1,679   219,56    0,95
  8.200   295,10   -1,847   212,64    0,99
  9.800   283,60   -2,043   207,01    1,12
 New buret
  0.700   238,00   -2,816   194,73    1,36
  1.980   196,40   -3,520   173,35    2,23
  4.020   169.90   -3,968   141,85    1.56
  7.200   144.80   -4,392    98,21   -0.63
 10.180   124.80   -4,731    62,35   -1,52
 12.000   110.90   -4,966    42,48   -1.94
 13.980    90.40   -5,314    22,39   -1,91
 New buret
  1.120    86.30   -5,384    19,34   -1.63
  2.200    82.00   -5,457    16,52   -1.35
  4.120    73.10   -5,609    11,76   -0,82
  5.120    67.80   -5,700     9,40   -0,44
  6.020    63.20   -5,779     7,34    0,18
* 7,120    62,80   -5,772     6,09    1,30
* 8,000    59,90   -5,822     4,20    2,35
*10,120    49,10   -6,009    -0,11    4,20
Sats 3  B=0.025M C=0.2M  Vo=30.70ml
  0.000   312.00   -1,325   248,10   -1,00
  1.400   308.20   -1,391   240,42   -0,03
  3,520   300.80   -1,520   229,98   -0,03
  5.400   292.70   -1,659   221,74   -0,20
  7.500   281.00   -1,859   213,51   -0.30
  9.400   265,90   -2,116   206,80   -0.27
 New buret
  1.120   203.10   -3,180   187,43    0.85
  2.300   178,80   -3.591   168,14    3,08
  4.100   156.10   -3,974   140,69    1.21
  6.100   140.20   -4,243   112,70    0,90
  8.200   125.90   -4,485    85,80    0.16
 10.300   111,70   -4,726    61,15   -0,64
 11,980    98,90   -4,942    42,85   -1,15
 14.000    78,80   -5,284    22,36   -0,91
 New buret
  1.200    74,50   -5,357    19,06   -0,62
* 3,020    68,60   -5,434    16,32   -0,97
* 4,500    63,20   -5,526    12,68   -0,19
* 5,800    58,90   -5,600     9,63    0,92
* 7,820    54,90   -5,668     6,89    2,07
* 9,100    48,30   -5,782     2,46    4,29
Sats 4  B=0.05M  C=0.2M  Vo=30.00ml
  0.000   318.10   -1.280   250,70    1.63
  0.700   315,80   -1.320   246,68    0,99
  2,100   311,20   -1,400   239,17    0,40
  4,100   304,20   -1,521   229,51    0,30
  6,400   293,80   -1,700   219,72   -0,22
  8,100   284,30   -1,862   213,24   -0,17
 10,100   269,10   -2,121   206,32    0,05
 New buret
  0.800   220.50   -2,944   192,44    1.02
  2.000   185.90   -3,530   172,61    1.12
  3.600   164.90   -3,885   147,86    0.84
  5.800   146.10   -4,203   116,65   -0.14
  8.000   130.80   -4,462    88,30   -1.26
 10.000   117.50   -4,687    64,68   -1,71
 12.000   102.30   -4,944    42,88   -2,31
 14.000    83.50   -5,263    22,68   -0,91
 New buret
* 2,000    78,40   -5,344    15,16    2,78
Sats 5  B=0.1M  C=0.2M  Vo=30.00ml
  0.000   320.00   -1,310   249,70   -0,87
  0.900   317.60   -1,351   244,57   -0,27
  3.100   310.10   -1,482   233,20   -0,50
  5.100   302.40   -1.614   224,10   -0,19
  7.100   292,50   -1,784   215,98   -0,12
  9.980   270,70   -2.155   205,72   -0,10
 New buret
  1.120   209.80   -3,186   186,37    0,39
  2.920   176.10   -3,756   157,39   -0,45
  5.020   157,90   -4,064   126,51    1,97
  8.020   136.10   -4,433    87,08    0,09
 11.020   115.40   -4,783    52,30   -0,83
 14.020    88,30   -5,243    21,37    0.17
*15,520    73,00   -5,484     8,53    3,33
*17,020    33,90   -6,160    -4,93    2,86
*18,520    -5,10   -6,910   -17,70   -3,43
*20,020   -14,80   -7,159   -29,83   -1,91
Sats 6  B=0.1M  C=0.2M  Vo=30.00ml
  0.000    84.50   -5,265    20,70   -0,11
  0.200    90.10   -5,170    25,01   -0,03
  0.600    98.30   -5.031    33,47   -0.62
  1.000   105.20   -4,914    41,71   -0,82
  2.000   119.10   -4,678    61,41   -0.23
  3.000   129,50   -4,502    79,91   -0.44
  4.000   138,90   -4,343    97,32    0.04
  6.000   156.40   -4,047   129,25    1.00
  8.180   177.60   -3,689   160,24    1.74
 10.000   202.80   -3,262   183,53    0.69
 11.200   238.20   -2,664   197,75    0.03
 12.000   270.20   -2.121   206,79   -0.50
 13.000   291.60   -1.756   217,60   -0,64
 14.000   303.20   -1.557   227,93   -0,58
 16.000   316.80   -1.322   247,24    0,22
 17.000   320.90   -1,250   256,28   -0.22
 18.000   324.30   -1.190   264,94   -0.55
 19.000   327.40   -1.135   273,24   -0.14
 20.000   329.90   -1.091   281,22   -0.19
Sats 7  B=0.1M  C=0.2M  Vo=30.00ml
  0.000   317.60   -1.289   251.10    0,26
  0.800   315.20   -1.331   246,42    0.09
  2.180   310.70   -1.409   239,36   -0.40
  3.800   305.10   -1,506   231,19   -0,29
  5.800   296.80   -1.649   222,45   -0.42
  8.100   284.50   -1.859   213,54   -0.40
 10.200   268.50   -2.131   206,29   -0.21
 New buret
  0.800   220.20   -2.950   192,45    0,37
  1.900   189.80   -3.464   174,28    1.33
  3.880   164.20   -3.897   143,86    1,16
  5.900   147.70   -4.176   115,52    0.65
  7.900   133.70   -4.412    89,80   -0.33
  9.900   120.30   -4.639    66,13   -1.10
 11.900   105.90   -4.883    44,29   -1.68
 13.900    88.13   -5.185    24,05    0.18
*14,900    85,20   -5.214    16,63    5,59
*15,440    77,20   -5.350    11,61    4,80
Sats 8  B=0.2M  C=0.2M  Vo=30.00ml
  0.000   335.10   -1.243   256,20    0.75
  0.800   332.70   -1.285   251,62    0.64
  4.200   322.40   -1.464   234,52   -0.51
  2.100   329.10   -1.348   244,65   -0.12
  6.200   315.40   -1.585   225,97   -0.49
  8.100   307.00   -1.729   218,68   -0.41
 10.060   296.70   -1.905   211,88   -0.32
 New buret
  1.040   242.20   -2.829   193,92    0.36
  2.040   211.70   -3.345   177,49    1.20
  3.440   190.10   -3.711   155,76    0.53
  5.020   175.00   -3.966   132,85    0.29
  7.020   160.10   -4.218   106,06   -0.34
  9.540   143.90   -4.492    75,38   -0.31
 12.240   124.20   -4.826    45,79   -1.94
 14.040   110.70   -5.054    27,70    0.62
*16,040    91,20   -5.372    10,34    2,96
*18,040    43,90   -6.190    -7,11   -0,06
*20,040    22.90   -6.575   -23,39    3,43
Sats 9  B=1.0M  C=0.1M  Vo=30.00ml
  0.000   326.80   -1.257   153,70    1.43
  0.600   324.20   -1.303   150,25   -0.64
  1.800   320.70   -1.364   143,73   -0.69
  3.600   315.00   -1.463   134,82   -0.66
  5.100   309.90   -1.551   128,10   -0.34
  7.600   299.10   -1.736   118,09   -0.31
 10.300   283.10   -2.009   106,67    0.03
 New buret
  0.800   265.00   -2.316   102,22    0.39
  2.900   216.60   -3.136    86,45    1.34
  5.000   192.50   -3.543    72,14    0.72
  7.320   175.20   -3.836    57,79   -0.08
 10.180   158.00   -4.127    41,92   -0.72
 14.020   134.10   -4.531    23,24   -1.60
*17,800   117,10   -4,808     8,22    4,12
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Table 1. For each titration are given: the total concentrations, E_0 estimated from a few acid points, the final value of E_0 and δH obtained in the refinement using LETAGROP.[9] Concentrations are given in M and emf values in mV. H is defined by: H (final) $= H$ [calculated from eqn. (2)] $+ \delta H$. H_0 is the value of H in the starting solution and H_T is the value of H in the buret solution [*cf.* eqn. (2)].

Titration No.	B	C	H_0	H_T 1st buret	2nd buret	3rd buret	E_0 from acid points	$E_0 \pm 3\sigma$	$(\delta H \pm 3\sigma) \times 10^3$
1	0.01	0.02	0.06925	−0.1061			391.8	391.5 ± 0.3	0.37 ± 0.27
2	0.01	0.2	0.2521	0.0738	−0.5020	−0.1259	404.2	404.6 ± 1.5	−1.2 ± 1.8
3	0.025	0.2	0.2482	0.0720	−0.5058	−0.1297	390.9	391.2 ± 1.7	−0.1 ± 2.2
4	0.05	0.2	0.2498	0.0736	−0.5042	−0.2028	395.7	394.7 ± 1.6	0.9 ± 2.2
5	0.1	0.2	0.2500	0.0738	−0.5040		397.9	398.3 ± 1.3	−0.3 ± 1.7
6[b]	0.1	0.2	0.0212	0.6725			395.6	395.8 ± 0.6	−0.5 ± 0.9
7	0.1	0.2	0.2504	0.0742	−0.5036		395.1	394.7 ± 1.0	0.6 ± 1.4
8	0.2	0.2	0.2554	0.0789	−0.4986		410.0	409.6 ± 1.0	0.8 ± 1.5
9	1.0	0.1	0.1540	−0.02220	−0.2220		401.7	402.1 ± 1.3	−0.3 ± 1.5

[b] = back titration.

SURVEY OF EXPERIMENTAL DATA

For each titration values of E_0, H_0, and H_T were calculated from the most acid points. $(V,E)_{B,C}$ with $[H^+] \geq 0.010$ M, by means of the computer program TRAVE.[7] The primary data were then transformed to $(H,h)_{B,C}$ (Table 1a) and $Z(\log h)_{B,C}$ (Fig. 1).

The total concentrations of iron(II) perchlorate $(=B)$ and ascorbic acid $(=C)$ were kept constant during each titration, but the analytical hydrogen ion concentration $(=H)$ was varied. In the initial and buret solutions $[H^+]_{tot}$ equals H_0 and H_T, respectively. The value of H in a solution prepared from V ml of buret solution and V_0 ml of starting solution is given by eqn. (2). Z was calculated from eqn. (3). In Table 1 we have given H_{calc} obtained from eqns. 4(a–d) with known equilibrium constants. Z_{calc} was calculated from eqn. (3) using the complexes and equilibrium constants finally obtained.

$$E = E_0 + 59.155 \log h - 17h \tag{1}$$

$$H = (V_0H_0 + VH_T)/(V_0 + V) \tag{2}$$

$$Z = (H - h + K_w h^{-1})/C \tag{3}$$

$$H = h + \sum p c_{pqr} \tag{4a}$$

$$B = b + \sum p c_{pqr} \tag{4b}$$

$$C = c + \sum r c_{pqr} \tag{4c}$$

$$\text{where } c_{pqr} = \beta_{pqr} h^p b^q c^r \tag{4d}$$

and K_w = the ionic product of water ($\log K_w = -14.22$ [2d])

TREATMENT OF THE DATA

The equilibria studied can be written as

$$p\text{H}^+ + q\text{Fe}^{2+} + r\text{HAsc}^- \rightleftharpoons \text{H}_p\text{B}_q\text{C}_r \tag{5}$$

In this study we have neglected the hydrolysis of Fe^{2+} (*cf.* Ref. 8). First we have treated the data for $\log h > -5.5$ (135 points in violet solution). Then a rough estimation of the complex formation for $\log h < -5.5$ (19 points in black solution) was made.

Complex formation in the range log h ≥ -5.5. As seen in Fig. 1 the effects are rather small. It is reasonable to assume that the complexes formed have the general formula $Fe_q(HAsc)_r$ (*cf.* Ref. 4). The data in Fig. 1 have been transformed to $Z_{C/B}$ ($\log c$), where $c = [HAsc^-]$ (*cf.* eqn. (6a) and Fig. 2). $Z_{C/B}$ ($\log c$) has been calculated in the same way as in Ref. 2a p. 1052.

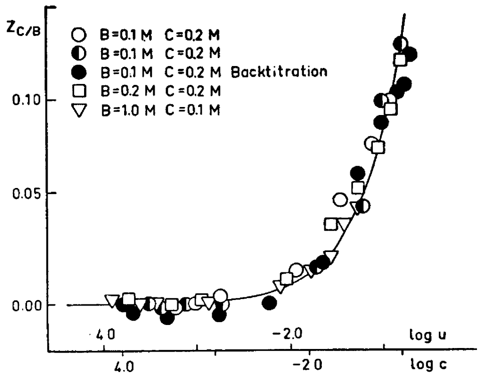

Fig. 2 $Z_{C/H}$ (= the average number of ascorbic acid molecules bound per B) as a function of $\log c$, where $c = [HAsc^-]$. The solid curve is the normalized function $u/(1+u)$ as a function of $\log u$ corresponding to $\log \beta_{011} = 0.20$.

$$Z_{C/B} = \sum r \beta_{pqr} b^q c^r / (b + \sum q \beta_{pqr} b^q c^r) \tag{6a}$$

$Z_{C/B}$ $(\log c)_{B,C}$ is independent of B (*cf.* Fig. 2). This indicates that $q = 1$ (*cf.* eqn. (6a)]. The experimental data can be very well explained by assuming one single iron ascorbate complex with $q = 1$ and $r = 1$, *i.e.* $FeHAsc^+$. By fitting the normalized curve $u/(1+u) = f(\log u)$ to the data, it was found that

$$\log \beta_{011} = 0.20 \pm 0.05 \tag{6b}$$

By using the least squares program LETAGROP,[9] minimizing $U = \sum(H_{calc} - H)^2$, we obtained

$$\log(\beta_{101} \pm 3\sigma) = 4.377 \pm 0.011 \tag{6c}$$

$$\log(\beta_{011} \pm 3\sigma) = 0.21 \pm 0.05$$

with $\sigma Z = 0.006$; where σ is the standard deviation, and (101) symbolizes H_2Asc. In the last refinement we have assumed small errors in H $(= \delta H)$ and E_0 $(= \delta E_0)$. The adjusted parameters δH indicate analytical errors of the expected order of magnitude (~0.5 %) and they show no trend. Moreover, the values of E_0 agree with those determined in acid solutions (by TRAVE [7]). (*cf.* Table 1b).

Complex formation in the range log h < -5.5. A few points (19) were taken in the range of acidity of the black solutions. The equilibria are slow in this range. No precipitate could be detected, however. For the most basic points stable emf values were obtained after about one hour. The effects are rather large and could be explained by assuming the presence of $FeHAsc^+$ together with at least one species of the type Fe_qAsc_r.

By assuming either FeAsc or Fe_3Asc_3 we obtained the following values:

$$\log(\beta_{\bar{1}11} \pm 3\sigma) = -6.58 \pm 0.09;\ \sigma Z = 0.009;\ U_Z = 12 \times 10^3 \qquad (6d)$$
$$\log(\beta_{\bar{3}33} \pm 3\sigma) = -16.98 \pm 0.19;\ \sigma Z = 0.011;\ U_Z = 17.10^3$$

Thus FeAsc gives the "best" fit with the data. The fit was not improved significantly if both FeAsc and Fe_3Asc_3 were assumed. The value of $\log \beta_{\bar{1}11}$ should be regarded as tentative, in view of the very limited experimental material available.

RESULTS AND DISCUSSION

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

$$\begin{aligned}&HAsc^- + H^+ \rightleftharpoons H_2Asc\\&\log(\beta_{101} \pm 3\sigma) = 4.377 \pm 0.011\\&Fe^{2+} + HAsc^- \rightleftharpoons FeHAsc^+\\&\log(\beta_{011} \pm 3\sigma) = 0.21 \pm 0.05 \qquad (7)\\&Fe^{2+} + HAsc^- \rightleftharpoons FeAsc + H^+\\&\log(\beta_{\bar{1}11} \pm 3\sigma) = -6.58 \pm 0.09\end{aligned}$$

Solutions with $\log[H^+] \geq -1.0$ containing the main species H_2Asc and Fe^{2+} are green or pale green. In solutions with $-1.0 > \log[H^+] > -5.5$ H_2Asc, $HAsc^-$, Fe^{2+}, and $FeHAsc^+$ predominate. These solutions are violet. At $\log[H^+] \sim -5.5$ the solution turns black. The data for $\log[H^+] < -5.5$ could be explained by assuming the formation of FeAsc. Since the equilibria are slow only a few points were measured and we cannot say anything definite about further complexes, $Fe_q(HAsc)_rH_p$, although the slowless of the equilibria imply that polynuclear complexes might well be formed.

Pfeilsticker[1c] has, by potentiometric titrations, determined a formal value $\log \beta_{\bar{1}11} = -5.8$ for FeAsc which would suggest a stronger complex than our value does. From IR measurements Pfeilsticker[1c] suggests that the complex is Fe_3Asc_3.

The value of pK_{a1} for ascorbic acid in this study agrees reasonably well with the value determined by us earlier, *viz.* $\log(\beta_{101} \pm 3\sigma) = 4.359 \pm 0.006$.[10] The distribution of ascorbic acid over the different species is shown in Fig. 3.

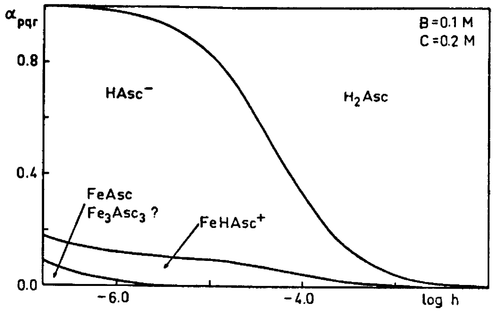

Fig. 3. The distribution of ascorbic acid on different species as a function of log *h*. $B = 0.1$ M and $C = 0.2$ M. The calculations have been performed by a computer program HALTAFALL[11] with the final equilibrium constants.

The complexes formed between L-ascorbate ions and Cd(II)[2a,b,c] as well as Ca(II)[2d,e] have been studied by our group. In those cases weak colourless complexes of type $Me_q(HAsc)_r$ are formed for $\log[H^+] \geq -5.5$, while at lower $\log[H^+]$ values yellow complex species of type Me_qAsc_r and Me_qAsc_rOH occur. Rather strong cadmium complexes with 3−5 Cd^{2+} and 3−6 ascorbic acid molecules predominate in solutions with $-5.5 \leq \log[H^+] \leq -8.5$. The cadmium complexes of ascorbic acid are stronger than the corresponding calcium species, which contain 3−4 Ca^{2+} and 3−4 ascorbic acid molecules and predominate at $-12.5 \leq \log[H^+] \leq -9.5$. The mononuclear complex CaAsc has been observed but not CdAsc.

The order of strength of the metal ascorbate complexes studied are $Cd^{2+} > Fe^{2+} > Ca^{2+}$. Ahrland, Chatt and Davies[12] have classified ligands and central atoms. Pearson[13] has introduced the terms soft and hard acids and bases. The term soft roughly characterises a high degree of polarization in the chemical bonds, while the term hard indicates a lower degree of polarization. The notation acids and bases are generalized to include central atoms (acids) and ligands (bases). Thus Cd^{2+} is classified as a soft acid, Ca^{2+} as a hard acid and Fe^{2+} as an intermediate acid. Soft acids in general bind soft bases stronger than hard bases. Binding oxygen atoms mostly constitute hard ligands.[12–14] However, in the case of ascorbic acid delocalized π-electrons probably give the ligand a rather soft character.

Thus, for all the metal ions studied we have found acid species $MeHAsc^{+}$ with weak interactions between the metal ions and the ascorbate ions. In more alkaline solutions, we have found stronger complexes, which are mainly polynuclear in solutions of Ca(II) and ascorbate and and in solutions of Cd(II) and ascorbate and probably also in solutions of Fe(II) and ascorbate ions. We have found evidence for small amounts of CaAsc and FeAsc but not for CdAsc. The trinuclear species Me_3Asc_3 seem to be important in the case of Ca(II) and Cd(II) and it might be so for Fe(II) too.

So far, it has not been possible to prepare crystals of metal ascorbates of type Me_qAsc_p. Hvoslef has investigated the structure of H_2Asc and $HAsc^-$ in the crystals of ascorbic acid and sodium ascorbate by X-ray and neutron diffraction methods.[15] He also has studied $Ca(HAsc)_2.2H_2O$.[15d] Hughes has determined the structure of TlHAsc.[16] These investigations do not contradict that three oxygen atoms in ascorbic acid may be available for the formation of tridentate chelated complexes as suggested by Pfeilsticker [1c] for the metal ascorbate complex Me_3Asc_3.

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