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Equilibrium Studies of L-Ascorbate Ions

V. Cadmium Ascorbate Complexes in Self Media Containing 3 M (Na,Cd)ClO_4 and Ascorbic Acid

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By potentiometric titrations using glass electrodes at 25°C we obtained 185 experimental points. Concentration ranges used: $0.4\ M \leq [Cd^{2+}]_{tot} \leq 1.4\ M$, $0.4 \leq [H_2Asc]_{tot} \leq 1.0\ M$ and $-3.4 \leq \log[H^+] \leq -0.8$, where H_2Asc = ascorbic acid.

These studies were confined to acid solutions to keep the activity coefficients constant, while allowing only for small changes in the medium.

The predominating species seem to be H_2Asc, $HAsc^-$, H_4Asc_2, $H_3Asc_2^-$, and $CdHAsc^+$. We also found evidence for $Cd_2H_3Asc_2^{3+}$.

The least squares program LETAGROP was used for selection and refinement of the final equilibrium model. In Table 3 are given the "best" values of the equilibrium constants.

In parts III[3] and IV[4] of this series we have studied the system $Cd^{2+} - HAsc^- - H^+$ at lower ascorbic acid concentrations ($C \leq 0.2$ M). We found that in acid solutions, where $HAsc^-$ is important, the predominating cadmium complex is $CdHAsc^+$ even in solutions where $B/C = 40$ or $C/B = 20$. In the present investigation we have studied complexes $Cd_q(HAsc)_rH_p$ in solutions with $B \geq 0.4$ M and $C \geq 0.4$ M. To keep the activity coefficients constant we restricted the Z-values to $0.85 \leq Z \leq 1.0$.

The equilibria treated in this article can be written

$$pH^+ (h) + q\ Cd^{2+} (b) + r\ C (c) \rightleftharpoons H_pB_qC_r (c_{pqr}) \quad (1)$$

SYMBOLS

The reactant symbols H, B, and C stand for H^+, Cd^{2+}, and ascorbic acid. Total concentrations are written H, B, C, and free concentrations h, b, c. H = the excess (analytical) concentration of H^+ over Cd^{2+}, H_2O, and C. For convenience we have chosen $C \equiv H_2Asc$ in the graphical treatment. In the

LETAGROP [7,8] calculation, however, we use C≡HAsc$^-$, as we did in parts III[3] and IV[4] of this series.

Z = the average number of H^+ bound per C. $C_{noB} = [H_2Asc] + [HAsc^-] + 2[H_4Asc_3] + 2[H_3Asc_2^-]$. (V,E) = volume and emf measured. A complete list of symbols is given in part II[2].

EXPERIMENTAL

The emf cell and the procedure of mixing solutions have been described in part II.[2] In this article the glass electrode is written as + pole. For description of chemicals, analysis, and apparatus we refer to part IV[4] and further references therein.

Notes on the emf measurements. 2 glass electrodes of type Beckman 41260 were used to measure $h = [H^+]$. The emf could be read off a few minutes after addition from the buret. The emf was always checked 5 min and 15 min after the addition. E was constant within ±0.1 mV.

In Fig. 1 is shown that the equilibria are reversible and reproducible.

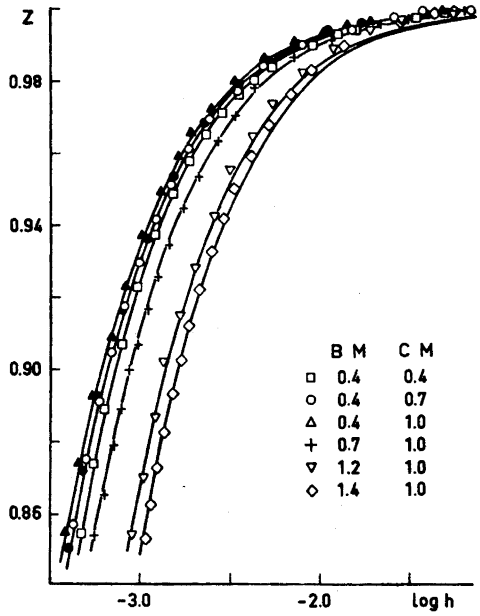

Fig. 1. $Z_{H/C}$ (= the average number of H^+ bound per C) as a function of log h. The solid curves were calculated, using HALTAFALL [6] and constants from eqn. (14). Filled symbols = back titrations.

SURVEY OF EXPERIMENTAL DATA

For each titration we have calculated E_0 and corrected H_0 or H_T using the computer program TRAVE [5] as described in part II[2].

The primary data $(V,E)_{B,C}$ have then been transformed to $(H,h)_{B,C}$ (Table 1 a) and Z (log $h)_{B,C}$ (Fig. 1). $h = [H^+]$ was calculated from eqn. (2). H and Z were calculated from eqns. (3) and (4). H_{calc} can be obtained from the general eqns. (5 a – c). Z_{calc} can then be calculated from eqn. (4), using H_{calc}. The total

Table 1 a. 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_T, and C_T, added to V_0 ml of a solution with total concentrations H_0, B_0, and C_0; E (≡"EA"); log $[H^+]$ (≡"LOGA"); H (≡"ATOT") and $(H_{calc}-H)$ 10^8 (≡"DATOT"). H_{calc} was calculated using the equilibrium constants in Table 3.

The systematic errors δH and the final values of E_0 are given in Table 1 b.

SATS 1 V_0= 30.0?

V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	295.30	-0.979	503.54	1.05
0.660	293.20	-1.017	495.97	-0.21
1.470	290.90	-1.059	487.12	-0.13
2.340	288.20	-1.107	478.10	-0.35
3.450	284.80	-1.167	467.28	0.25
4.350	281.40	-1.227	459.02	-0.34
5.340	277.70	-1.292	450.25	0.11
7.430	268.20	-1.457	433.76	0.15
9.330	256.30	-1.662	420.15	0.07
10.270	248.70	-1.792	413.89	0.16
10.890	243.00	-1.890	410.17	0.12
11.640	234.10	-2.041	405.27	0.15
12.250	226.60	-2.169	401.62	0.27
12.700	220.80	-2.267	398.99	0.30
13.130	215.20	-2.362	396.52	0.25
13.570	209.90	-2.452	394.05	0.22
14.050	204.80	-2.538	391.42	0.26
14.600	199.20	-2.633	388.46	0.03
15.240	194.00	-2.721	385.12	0.00
16.030	188.50	-2.814	381.12	-0.10
17.010	182.90	-2.909	376.34	-0.23
18.310	177.00	-3.009	370.30	-0.29
19.790	171.70	-3.099	363.81	-0.25
21.670	166.20	-3.192	356.30	-0.54
23.110	162.70	-3.251	350.57	-0.42
25.040	158.70	-3.318	343.61	-0.53

SATS 2 V_0= 30.0?

V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	313.10	-0.810	853.41	1.08
0.700	310.60	-0.857	838.54	0.08
1.490	307.70	-0.911	822.56	-0.15
2.250	304.70	-0.965	807.92	-0.16
3.000	301.60	-1.022	794.14	0.41
3.700	298.10	-1.085	781.83	-0.18
4.480	294.20	-1.154	770.01	-0.65
5.150	289.90	-1.230	757.72	0.24
5.810	285.40	-1.309	747.62	0.37
6.510	279.70	-1.408	737.15	0.52
7.510	269.10	-1.591	722.87	0.62
8.410	255.60	-1.822	710.65	0.75
9.170	239.40	-2.098	700.76	0.35
9.770	226.20	-2.322	693.23	0.16
10.270	217.90	-2.463	687.12	0.75
10.820	208.60	-2.620	680.58	-0.22
11.370	201.90	-2.734	674.21	-0.57
12.020	196.30	-2.829	666.89	0.01
12.670	191.20	-2.915	659.80	-0.09
13.470	186.00	-3.003	651.36	-0.21
14.330	181.20	-3.084	642.63	-0.63
15.230	177.20	-3.152	633.85	-0.50
16.280	173.10	-3.221	624.03	-0.62
17.550	168.90	-3.292	612.92	-0.87
19.040	164.80	-3.361	600.24	-0.53

SATS 3 V_0= 36.3?

V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	163.20	-3.389	594.66	-0.28
1.210	168.00	-3.308	609.70	-0.41
2.440	173.20	-3.220	624.30	-0.76
4.010	180.60	-3.095	641.21	-0.55
5.410	188.20	-2.967	655.45	-0.60
6.720	196.90	-2.819	667.98	-0.36
7.970	207.30	-2.643	679.27	-0.17
8.970	218.10	-2.460	687.87	0.12
9.720	227.80	-2.296	694.08	0.26
10.470	238.20	-2.119	700.11	0.29
11.230	248.10	-1.951	706.03	0.25
12.230	258.80	-1.768	713.55	0.26
13.830	270.70	-1.564	724.98	0.26
15.730	279.80	-1.407	737.67	0.08
17.750	286.70	-1.287	750.22	0.36
19.480	290.90	-1.213	760.27	0.03
21.340	294.70	-1.146	770.43	0.25
23.240	297.80	-1.091	780.17	0.28
25.350	300.70	-1.039	790.31	0.54
27.550	303.00	-0.997	800.19	-0.11
29.910	305.20	-0.957	810.07	-0.25
32.770	307.60	-0.913	821.18	0.44
36.770	310.10	-0.867	835.29	0.08

SATS 4 V_0= 34.53

V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	174.00	-3.396	853.71	2.34
1.250	178.00	-3.328	872.97	-0.04
2.500	182.50	-3.252	891.07	-1.06
3.750	188.30	-3.154	908.13	1.14
4.850	192.90	-3.076	922.35	0.15
6.020	197.90	-2.992	936.72	-1.69
7.110	204.10	-2.887	949.46	+1.25
8.010	210.00	-2.787	959.54	-0.90
8.610	214.50	-2.711	966.05	-0.62
9.310	220.40	-2.611	973.44	-0.39
10.120	228.20	-2.479	981.74	-0.41
10.920	238.00	-2.313	989.67	0.01
11.620	247.40	-2.153	996.40	0.01
12.270	257.20	-1.987	1002.49	0.54
12.920	265.50	-1.845	1008.43	0.57
13.620	273.00	-1.717	1014.67	0.58
14.520	281.20	-1.576	1022.45	1.22
16.020	289.70	-1.430	1034.85	0.30
17.520	296.10	-1.318	1046.60	-0.13
18.830	300.70	-1.238	1056.37	0.16
20.530	305.30	-1.157	1068.41	0.23
23.540	311.30	-1.050	1088.14	0.22
26.040	315.00	-0.983	1103.15	0.17
28.040	317.30	-0.941	1114.36	-0.43
30.550	319.90	-0.893	1127.52	-0.19
34.560	323.10	-0.834	1146.70	-0.52

SATS 5 V_0= 30.0?

V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	329.30	-0.809	1154.63	-0.05
0.550	327.70	-0.839	1144.69	-0.55
1.150	325.90	-0.872	1134.26	-0.94
1.750	324.20	-0.904	1124.22	-0.33
2.350	322.30	-0.939	1114.55	-0.36
3.000	320.10	-0.979	1104.48	-0.54
3.750	317.30	-1.029	1093.33	-1.08
4.460	314.80	-1.074	1083.23	-0.28
5.160	311.90	-1.126	1073.67	-0.35
5.960	308.20	-1.192	1063.20	-0.60
6.810	304.30	-1.260	1052.57	0.33
7.810	298.30	-1.365	1040.68	-0.09
9.010	289.90	-1.511	1027.21	0.08
10.020	281.20	-1.660	1016.50	0.34
10.870	271.90	-1.819	1007.90	0.05
11.520	264.80	-1.941	1001.56	0.43
12.520	252.10	-2.157	992.19	+0.61
13.770	240.90	-2.347	981.07	-0.04
14.780	233.30	-2.475	972.54	-0.29
15.780	227.60	-2.572	964.47	-0.07
17.130	221.20	-2.680	954.11	-0.19
18.380	216.30	-2.763	945.04	-0.56
19.890	211.80	-2.839	934.68	-0.14
21.290	208.10	-2.902	925.62	-0.27
22.790	204.80	-2.958	916.45	-0.13
24.540	201.70	-3.010	906.39	0.67
26.290	198.70	-3.061	896.96	0.39
28.040	196.10	-3.105	888.09	0.20
30.050	193.70	-3.146	878.54	0.85
33.050	190.70	-3.196	865.43	2.08
36.060	187.90	-3.244	853.46	2.17

SATS 6 V_0= 30.0?

V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	332.30	-0.793	1160.13	-0.27
0.400	330.30	-0.822	1150.17	-0.54
1.000	328.40	-0.866	1135.72	+1.01
1.650	325.80	-0.914	1120.68	-0.37
2.400	322.70	-0.971	1104.07	1.13
3.100	319.10	-1.036	1089.25	0.79
3.800	315.00	-1.110	1075.05	0.33
4.460	310.70	-1.186	1062.18	0.23
5.110	306.30	-1.263	1049.98	1.25
5.760	300.60	-1.363	1038.23	0.99
6.760	289.90	-1.548	1020.96	1.04
7.510	279.80	-1.722	1008.61	1.04
8.310	267.30	-1.935	995.97	0.56
9.020	257.00	-2.110	985.18	0.33
9.770	247.60	-2.270	974.21	-0.34
10.520	240.10	-2.397	963.64	-0.97
11.270	233.20	-2.514	953.46	-3.20
12.270	228.00	-2.602	940.44	-1.19
13.520	221.80	-2.707	925.01	-1.09
14.680	217.20	-2.785	911.46	-0.66
15.840	213.20	-2.852	898.71	+0.65
17.330	208.90	-2.925	883.01	+0.13
19.040	205.00	-2.991	866.28	1.43
20.790	201.30	-3.054	850.32	1.69

SATS 7 V_0= 30.0?

V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	333.20	-0.805	1158.44	-3.22
0.540	332.10	-0.826	1148.24	-0.37
1.150	330.40	-0.858	1137.89	-0.66
1.800	328.80	-0.887	1126.94	1.02
2.450	326.80	-0.924	1116.42	0.86
3.200	324.30	-0.970	1104.79	0.40
4.000	321.70	-1.017	1092.96	0.99
4.760	318.90	-1.067	1082.22	0.93
5.510	316.00	-1.119	1072.07	1.14
6.370	312.20	-1.187	1060.95	0.87
7.260	308.00	-1.260	1049.98	1.06
8.510	301.10	-1.381	1035.43	1.09
10.020	290.90	-1.557	1019.07	1.07
11.270	280.50	-1.736	1006.43	0.61
12.270	272.00	-1.881	996.86	0.61
13.570	261.30	-2.063	985.51	-0.32
14.530	254.30	-2.182	976.80	-0.62
15.780	247.10	-2.304	966.56	-1.08
17.030	241.10	-2.406	956.86	-1.83
18.380	236.00	-2.492	946.95	-2.18
19.620	232.20	-2.557	938.33	-2.14
21.040	228.80	-2.614	928.96	-1.23
22.790	224.70	-2.684	918.11	+1.63
24.540	221.30	-2.741	907.96	+1.74
26.340	218.60	-2.787	898.18	-0.76
28.240	215.90	-2.833	888.50	-0.49
30.500	213.20	-2.878	877.79	0.21
32.750	210.90	-2.917	867.89	1.06
35.240	208.80	-2.953	857.65	2.63
37.810	206.70	-2.988	848.02	3.18

Table 1 b. For each titration are given: the total concentrations, E_0 estimated from a few acid points, the final value of E_0, j, and δH obtained in the refinement of the equilibrium model (from LETAGROP). Concentrations are in M, and emf values in mV.

Titration No.	B	C	H_0	H_T	E_0 (from acid points)	$E_0 \pm 3\sigma$ (refined)	$j \pm 3\sigma$	$10^3(\delta H \pm 3\sigma)$
1	0.4	0.4	0.5028	0.1512	355.3	355.0± 0.2	−17.5± 1.8	0.7± 0.4
2	0.4	0.7	0.8526	0.2004	363.9	363.7± 0.2	−17.4± 0.5	0.8± 0.6
3	0.4	0.7	0.5956	1.0870	363.6	363.7± 0.2		−0.9± 0.6
4	0.4	1.0	0.8550	1.4831	374.7	374.9± 0.4	−17.7± 0.4	−1.3± 1.2
5	0.7	1.0	1.1549	0.6031	379.8	379.8± 0.3	−17.5± 0.6	−2.7± 0.8
6	1.2	1.0	1.1645	0.4075	381.4	381.9± 0.4	−17.5± 0.9	−4.4± 1.1
7	1.4	1.0	1.1634	0.6066	382.7	383.5± 0.7	−18.3± 1.1	−4.9± 2.4

concentrations in the buret solution $= H_T$, B_T, C_T and the total concentrations in the equilibrium solution $= H_0$, B_0, C_0 are known from analyses.

$$E = E_0 + 59.155 \log h + E_j \qquad E_j = -17\,h \qquad (2)$$

$$H = (V_0 H_0 + V H_T)/(V_0 + V) \qquad (3\text{ a})$$

$$B = B_0 = B_T \qquad (3\text{ b})$$

$$C = C_0 = C_T \qquad (3\text{ c})$$

$$Z = (H - h + K_w h^{-1})/C \,^a \qquad (4)$$

$$H = h + \sum p\beta_{pqr} h^p b^q c^r \qquad (5\text{ a})$$

$$B = b + \sum q\,\beta_{pqr} h^p b^q c^r \qquad (5\text{ b})$$

$$C = c + \sum r\,\beta_{pqr} h^p b^q c^r \qquad (5\text{ c})$$

[a] $K_w h^{-1} = [OH^-] \approx 0$.

TREATMENT OF DATA

The hydrolysis of Cd(II) was neglected [6], since $\log h > -3.4$ for all experimental points.

In the graphical treatment we have chosen H_2Asc, H^+ and Cd^{2+} as components. This is practical, since Cd^{2+}, H_2Asc, and H_4Asc_2 are present in high and constant concentrations.

In the LETAGROP [7,8] calculations we chose $HAsc^-$, H^+, and Cd^{2+} as components for the sake of conformity (same as in parts III[3] and IV[4]).

Graphical treatment

The medium contains both B and C. The complexes can then formally be written H_p (*cf.* part II[2]). Some general equations:

$$H-h=\sum pc_{pqr} \quad (6\ a)$$

$$c_{pqr}=K_p h^p \quad (6\ b)$$

$$K_p=\sum \beta_{pqr} b^q c^r \quad (6\ c)$$

where b and c are approximately constant.

1. Determination of $\bar{p}$ = the average value of p in the complexes. By definition

$$\bar{p}=\sum pc_{pqr}/\sum c_{pqr} \quad (7)$$

Differentiation of (6 b) and insertion of (6 a) followed by integration gives

$$\sum c_{pqr}=\int_{\log h_0}^{\log h}(H-h)\,\mathrm{d}\log h \quad (8)$$

Eqns. (6 a), (7) and (8) give:

$$\bar{p}=(H-h)/\left(\int_{\log h_0}^{\log h}(H-h)\,\mathrm{d}\log h\right) \quad (9)$$

From eqn. (9) $\bar{p}$ was calculated by graphical integration using the trapezoid formula. The result is shown in Fig. 2:

$$\bar{p}=-1.0\pm 0.2$$

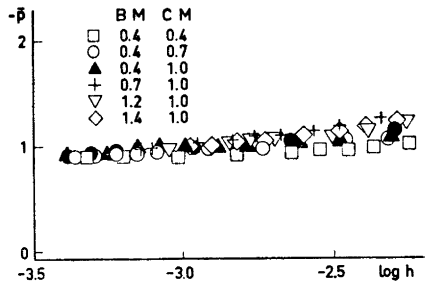

Fig. 2. $\bar{p}$ (= the average number of $[H^+]$ per complex) as a function of log h.

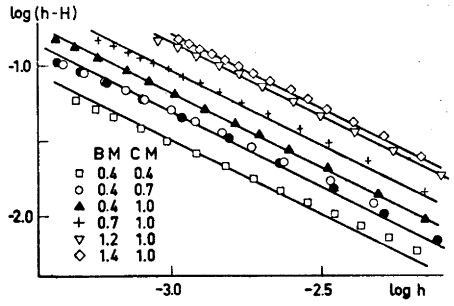

Fig. 3. Log $(h-H)$ as a function of log h. Filled symbols = back titrations. The solid lines correspond to eqn. (10) with $K_{\bar{1}}$ from Table 2.

2. Determination of monoligandic constants $K_{\bar{1}}$. From eqns. (6 a–b) we get $h-H=K_{\bar{1}}h^{-1}$ $(p=-1)$. Taking the logarithm gives

$$\log\,(h-H)=-\log h+\log K_{\bar{1}} \quad (10)$$

For constant B and C, log $(h-H)$ as a function of log h is a straight line. The slope is -1 and the intercept at log $h=0$ is log $K_{\bar{1}}$ (Fig. 3). From the best fit of lines in Fig. 3 we obtain $K_{\bar{1}}$ for each pair (B,C). The values of $K_{\bar{1}}$ are found in Table 2.

Table 2. Analysis of $K_{\bar{1}} = (h-H)\,h = [HAsc^-]\,h + [H_2Asc_2^-]\,h + \sum [Cd_q(H_2Asc)_r H_p]\,h$. $K'_{\bar{1}} = \sum [Cd_q(H_2Asc)_r H_p]\,h$. $b \approx B$ and $c = [H_2Asc]$ is estimated from eqn. (10).

B M ($b \approx B$)	C M	$K_{\bar{1}} \times 10^4$	$[H_2Asc] = c$	$[HAsc^-]h \times 10^4$	$[H_2Asc_2^-]h \times 10^4$	$K'_{\bar{1}} \times 10^4$	$\beta_{011} = \frac{K'_{\bar{1}}}{b\,c} \times \beta_{101}$
0.4	0.4	0.302	0.271	0.123	0.043	0.136	2.75
0.4	0.7	0.490	0.416	0.190	0.102	0.198	2.63
0.4	1.0	0.676	0.536	0.245	0.169	0.262	2.67
0.7	1.0	0.955	0.540	0.247	0.172	0.536	3.11
1.2	1.0	1.413	0.545	0.249	0.175	0.989	3.31
1.4	1.0	1.622	0.550	0.251	0.178	1.193	3.39

3. Analysis of $K_{\bar{1}}$ (b,c). From eqn. (6) we get the amount of H^+ bound in complexes as

$$H - h = K_{\bar{1}}\,h^{-1} \text{ where } K_{\bar{1}} = \sum \beta_{\bar{1}qr}\,b^q c^r$$

We approximate $b = B$, and estimate $c = [H_2Asc]$ from eqns. (11 a – b).

$$2[H_4Asc_2] + [H_2Asc] = C \qquad (11\ a)$$

$$[H_4Asc_2] = 0.69\ [H_2Asc]^2 \qquad (11\ b)$$

Eqn. (11 b) concerns the equilibrium $2H_2Asc \rightleftharpoons H_4Asc_2$. The constant $= 0.69$ was obtained in part I.[1]

As a first approximation we assume $CdHAsc^+$ to be the only cadmium complex present in the solution (Table 2). We subtracted the contribution to $H - h$ from $HAsc^-$ and $H_3Asc_2^{2-}$, taking the necessary equilibrium constants from part I[1]. The calculated formation constant for $CdHAsc^+$ $= \beta_{011}$ varies a little when B is increased from 0.4 to 1.4, but seems roughly independent of C. Because of the approximations introduced and the small variation of β_{011} with B it is difficult to say anything about complexes with higher q- or r-values. The predominant equilibrium for Cd(II) seems to be

$$Cd^{2+} + HAsc^- \rightleftharpoons CdHAsc^+ \text{ with } \beta_{011} = 3.0 \pm 0.4$$

Calculations using LETAGROP

Selection of complexes. From the graphical treatment we know that the main Cd(II) species can be written $Cd_q(H_2Asc)_r[H^+]_{\bar{1}}$ or $Cd_q(H_2Asc)_{r-1}HAsc$. The pure ascorbic acid species we know from part I.[1] They are (101), (102), and (202). The graphical treatment indicates $CdHAsc^+$ to be present.

The apparent value of β_{011} was now calculated, using LETAGROP [7,8] minimizing $U_s = (Z_{calc} - Z)^2$. The primary data $(V,E)_{B,C}$ were used directly without any approximations. Each medium, thus with constant (B,C) was treated separately. As seen in Fig. 4, β_{011}' increases with increasing B. This can be explained by a model containing the complex $Cd_Q(H_2Asc)_{K-1}HAsc$ with $Q > 1$ thus:

$$(101)+(102)+(202)+(011)+(R-1, Q, R) \qquad (12\ a)$$

1. The value of Q. The amount of C bound in the complexes with cadmium (II) can be written:

$$C-C_{noB}=\sum r\ \beta_{pqr}\ h^p b^q c^r \qquad (12\ b)$$

If we introduce $[H_2Asc]=\beta_{101}hc$ and $b\approx B$ in (12 b) and assume that $CdHAsc^+$ and $Cd_Q(H_2Asc)_{R-1}HAsc$ are present (12 b) can be written:

$$C-C_{noB}=r\ \beta'_{011}\ B\ c$$

where

$$\beta'_{011}=\beta_{011}+\beta_{R-1,Q,R}\times\beta_{101}^{-1}\times B^{Q-1}\times[H_2Asc]^{R-1}$$

In Fig. 4 we have plotted β'_{011} obtained from LETAGROP calculations against B at constant $C=1$ M. Since $[H_2Asc]$ is a constant, we obtain:

$$\beta'_{011}=\beta_{011}+\text{const.}\ B^{Q-1} \qquad (12\ c)$$

β'_{011} can be described by a linear function (Fig. 4), indicating that $Q=2$.

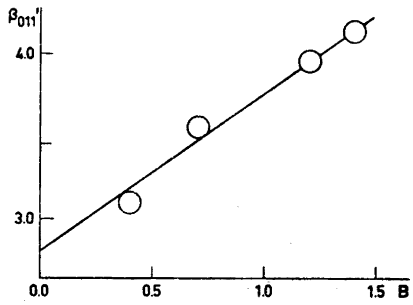

Fig. 4. β'_{011} = the apparent formation constant for $CdHAsc^+$ as a function of B. The solid line corresponds to $\beta'_{011}=1.0\ B+2.9$.

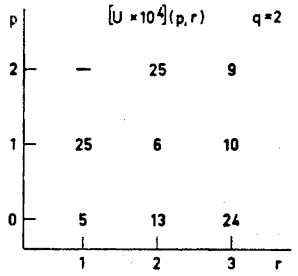

Fig. 5. $U_z=\sum(Z_{calc}-Z)^2$ as a function of p and r. $q=2$.

Table 3. Results of LETAGROP calculations, using all points (185), minimizing $U_z=\sum(Z_{calc}-Z)^2$. The final result is given in italics.

$U\times10^5$	(δZ)	$\log(\beta_{pqr}\pm3\sigma)$ $(pqr)=(101)$	(102)	(202)	(011)	(122)	The systematic errors
246	0.0037	4.34_2	4.45	8.56	0.56 ± 0.02	—	$\delta E_0=0$, $\delta H=0$
169	0.0030	4.34_2	4.45	8.56	$0.56_5\pm0.010$	—	δE_0 and δH adjusted
60	0.0018	4.34_2	4.45	8.56	$0.47_2\pm0.009$	4.67 ± 0.02	$\delta E_0=0$, $\delta H=0$
30	0.0013	4.34_2	4.45	8.56	$0.47_8\pm0.006$	$4.66_7\pm0.007$	δE_0 and δH adjusted
51	0.0017	$4.34_3\pm0.010$	4.26 ± 0.03	8.49 ± 0.01	$0.49_2\pm0.005$	$4.55_0\pm0.002$	$\delta E_0=0$, $\delta H=0$
16	*0.0009*	*4.363 ± 0.019*	*4.28 ± 0.09*	*8.483 ± 0.003*	*0.502 ± 0.006*	*4.665 ± 0.002*	*δE_0 and δH adjusted*

Notes. Values obtained in part I;[1] $\log\beta_{101}=4.359\pm0.006$, $\log\beta_{102}=4.45\pm0.04$, and $\log\beta_{202}=8.56\pm0.05$. The equilibrium constants were not varied at the same time as systematic errors were adjusted (*cf.* part I[1]).

2. The value of R. Determination of β_{PQR}. To determine the most probable value of R we have calculated $U_z = \sum(Z_{calc} - Z)^2$ for different combinations $(101)+(102)+(202)+(011)+(PQR)$, where $0 \leq P \leq 2$, $Q=2$, and $1 \leq R \leq 3$. As seen in Fig. 5 we got low U_z-values for (021) and (122), corresponding to $Cd_2(H_2Asc)\ HAsc^+$ and $Cd_2(H_2Asc)_2HAsc^{3+}$. C varied between 0.4 and 1.0 M, and $c = [H_2Asc]$ between 0.3 and 0.6 M. To get a broader range of C we used data from part IV[4] and picked out 134 points with C in the interval $0.002 \leq C \leq 1.0$ M. Now (021) and (122) were tested minimizing U_z using $\log \beta_{101} = 4.36$, $\log \beta_{102} = 4.45$, and $\log \beta_{202} = 8.56$ from part I.[1] We obtained:

$$\log(\beta_{011} \pm 3\sigma) = 0.39 \pm 0.04 \qquad \log(\beta_{021} \pm 3\sigma) = -0.81 \pm 0.5$$
$$\sigma(Z) = 0.0084 \qquad \text{(12 d)}$$
$$\text{or} \quad \log(\beta_{011} \pm 3\sigma) = 0.42 \pm 0.02 \qquad \log(\beta_{122} \pm 3\sigma) = 4.66 \pm 0.06$$
$$\sigma(Z) = 0.0055$$

Thus $CdHAsc^+$ and $Cd_2H_3Asc_2^{3+}$ ($R=2$) give the "best" fit with the data. The final model is:

$$(101)+(102)+(202)+(011)+(122) \qquad \text{(12 e)}$$

Refinement by least squares treatment (LETAGROP)

The final model (12 e) was refined minimizing $U_z = \sum (Z_{calc} - Z)^2$, using 185 points with $0.4\ M \leq [Cd^{2+}]_{tot} \leq 1.4$ M, and $0.4\ M \leq C \leq 1.0$ M. The values of β_{101}, β_{011}, β_{202}, and β_{102} (Table 3) agree well with those obtained earlier in parts I,[1] III,[3] and IV.[4] Systematic errors δH and δE_0 were treated as parameters. We assumed analytical errors in $H = \delta H$, and small errors in $E_0 = \delta E_0$:

$$\text{Final } H = H \text{ (calculated from analysis, } cf. \text{ part II}^2) + \delta H \qquad \text{(13)}$$
$$\text{Final } E_0 = E_0 \text{ (calculated from a few acid points, } cf. \text{ part II}^2) + \delta E_0$$

We also checked the liquid junction potential. The values of δH, final E_0, and $j = E_j/h$ obtained are given in Table 1 b.

The error, $\delta H = -4.9$ mM for $B = 1.4$ M and $C = 1.0$ M, seems high but not unreasonably so ($= 1.6$ % in H). We obtained the liquid junction potential $= (-17._5 \pm 1)h$. E_j seems independent of B and C in the present ionic media.

RESULT AND DISCUSSION

As the final result we propose the following reactions and constants valid in 3 M $(Na,Cd)ClO_4$ media at 25°C:

	pqr	Reaction	($\log \beta_{pqr} \pm 3\sigma$)	
1.	101	$HAsc^- + H^+ \rightleftharpoons H_2Asc$	4.36 ± 0.02	
2.	102	$2HAsc^- + H^+ \rightleftharpoons H_3Asc_2^-$	4.28 ± 0.09	
3.	202	$2HAsc^- + 2H^+ \rightleftharpoons H_4Asc_2$	8.48 ± 0.01	(14)
4.	011	$Cd^{2+} + HAsc^- \rightleftharpoons CdHAsc^+$	0.50 ± 0.01	
5.	122	$2Cd^{2+} 2HAsc^- + H^+ \rightleftharpoons Cd_2H_3Asc_2^{3+}$	4.67 ± 0.01	

The solutions contain the pure ascorbic acid species H_2Asc, $HAsc^-$, $H_3Asc_2^-$, and H_4Asc_2. The predominating cadmium species is $CdHAsc^+$. Probably $Cd_2H_3Asc_2^{3+}$ is also present in the solution. The final model agrees very well with our result in parts I,[1] III,[3] and IV[4] in this series.

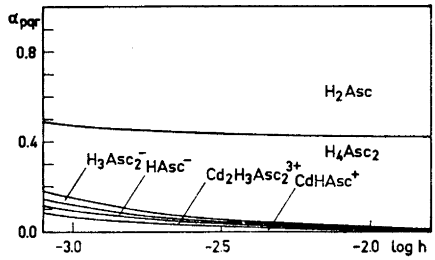

Fig. 6. The distribution of ascorbic acid on different species as a function of log h. $B = 1.2$ M, $C = 1.0$ M. HALTAFALL [6] was used for the calculations, taking the constants from Table 3. At a given value of log h the fraction of ascorbic acid present as $H_pB_qC_r$ is represented by the segment of a vertical line falling within the corresponding area.

A distribution diagram of ascorbic acid on different species, calculated using HALTAFALL,[9] is shown in Fig. 6. Veselinović and Sušić [11] have found that $CdHAsc^+$ is the most important Cd(II) species in acid solutions. Their value, log $\beta_{011} = 1.3$, was obtained by extrapolation to zero ionic strength.

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