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Equilibrium Studies of L-Ascorbate Ions

IV. Equilibria between Cadmium(II) Ions, Ascorbate Ions, and Protons in Perchlorate Self Medium

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Data were collected by potentiometric titrations at 25°C, using glass electrodes. The titrations yielded 420 experimental points. The concentration ranges used: $0.4 \leq [Cd^{2+}]_{tot} \leq 1.4$ M, $0.002 \leq [H_2Asc]_{tot} \leq 0.08$ M and $-6.5 \leq \log [H^+] \leq -1.0$ M, where $H_2Asc \equiv$ ascorbic acid.

In acid solutions, where $-4.5 \leq \log h \leq -1.0$, our data indicate the main species to be H_2Asc, $HAsc^-$ and $CdHAsc^+$.

In neutral solutions, where $-6.5 \leq \log h \leq -4.5$, the most important species seem to be $HAsc^-$, $CdHAsc^+$, Cd_2Asc^{2+}, and Cd_4Asc_4. We also found evidence for $Cd_5Asc_4OH^+$, Cd_3Asc_3, and $Cd_3Asc_3OH^-$ (*cf.* part III), The least squares program LETAGROP was used to select and refine the final equilibrium model. In Table 5 are given the "best" values of the equilibrium constants.

In connexion with our studies on the system $Cd^{2+}-HAsc^--H^+$ in the concentration interval $0.00125 \leq B \leq 0.2$ M, and $0.005 \leq C \leq 0.2$ M in part III [3] we have now investigated the same system at higher cadmium concentrations. We were interested to know, *e.g.*, if Cd_4Asc_4 is important at high cadmium concentrations and if any species with two Cd^{2+} is formed. The equilibria studied can be written:

$$pH^+(h) + qCd^{2+}(b) + rHAsc^-(c) \rightleftharpoons H_pB_qC_r(c_{pqr}) \quad (1)$$

SYMBOLS

The notations H, B, C, stand for the reactants H^+, Cd^{2+} and $HAsc^-$. Total concentrations are written H, B, C, and the free concentrations h, b, c. $H \equiv$ the excess (analytical) concentration of H^+ over Cd^{2+}, H_2O, and $HAsc^-$. $Z =$ the average number of H^+ bound per C. $Z_{C/B} =$ the average number of C bound per B. $Z^* = Z$ corrected for the hydrolysis of Cd^{2+}.

$C_{\text{noB}} = c + \sum r[\text{H}_p\text{C}_r]$, $C_{\text{noB}}Z_{\text{noB}} = \sum p[\text{H}_p\text{C}_r]$, $B_{\text{noC}} = b + \sum q[\text{Me}_q(\text{OH})_n]$, $B_{\text{noC}}Z_{\text{noC}} = \sum p[\text{Me}_q(\text{OH})_n]$. (V,E) = volume and emf measured. A complete list of symbols is given in part II.[2]

EXPERIMENTAL

Chemicals and analyses. Solutions of $NaClO_4$, $HClO_4$, NaOH, L-ascorbic acid and NaCl were prepared and analysed as in part I [1] and part III.[3]

$Cd(ClO_4)_2$ was prepared and analysed as in part III.[3] The analyses for Cd^{2+} were mostly carried out as electrolyses in a KCN solution.

Apparatus. Saltbridge, electrodes, potentiometer and thermostat have been described in part II [2] and part III.[3]

Notes on the emf measurements. The construction of the measuring cell and the procedure of mixing solutions were described in part II.[2] In this article the glass electrode is written as + pole.

In the experiments, we used 4 different glass electrodes picked out from 5 Beckman 41260 electrodes.

The emf became stable within 5 min, except for the most basic points, where we often had to wait 30 min to get stable emf values.

Titrations with $C = 0.002$ M and $B = 0.4$ M gave stable emf values only for log $h > -4.5$.

Figs. 1 and 2 show that the reproducibility is very good. The reversibility of the equilibria was checked by back titrations.

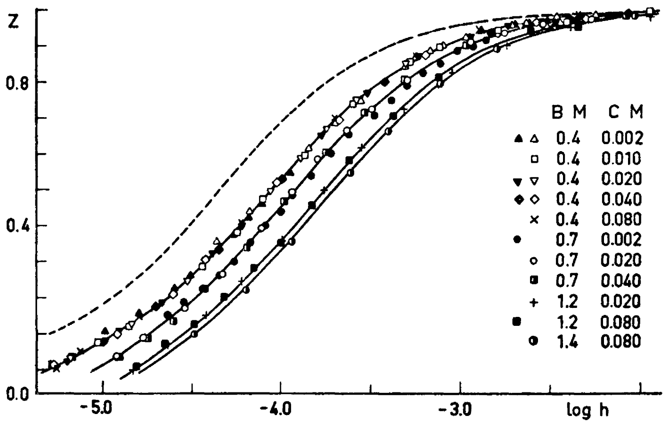

Fig. 1. Z (= the average number of H^+ bound per C) as a function of log h. The full curves are normalized functions $[V/(1+V)](\log V)$ corresponding to log $\beta_{101} = 4.36$ and log $\beta_{011} = 0.41$. Back titrations are marked with filled symbols. The dashed line corresponds to the Z-curve for ascorbic acid when Cd(II) is absent.

SURVEY OF EXPERIMENTAL DATA

For each titration we have calculated E_0 and corrected H_0 or H_T using the computer program TRAVE,[4] 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 $Z(\log h)_{B,C}$ (Figs. 1 and 2). $h = [H^+]$ was calculated from E = emf measured (eqn. 2). H has been obtained from eqn. (3 a). From analyses we know the total con-

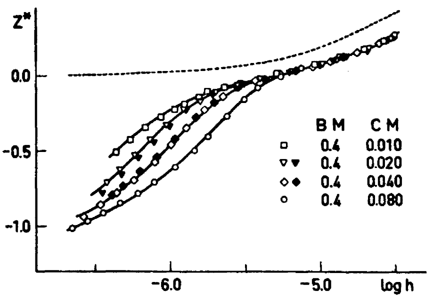

Fig. 2. Z^* (= the average number of H^+ bound per C) as a function of log h. The full curves have been calculated using HALTAFALL [5] and the constants in Table 5. Filled symbols represent back titrations. The dashed line corresponds to the Z-curve for ascorbic acid when Cd(II) is absent.

centrations in the buret solution $= H_T$, B_T, C_T and in the first starting equilibrium solution $= H_0$, B_0, C_0. Z was calculated from eqn. (4). For the graphical treatment we use Z^*, obtained by introducing a small correction for $Cd_q(OH)_n$ in Z (eqn. (6)). H_{calc} can be calculated from the general eqns. (5 a – c), and then Z_{calc} from eqn. (4).

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

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

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

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

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

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

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

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

$$Z^* = Z - B_{noC} Z_{noC}/C \qquad (6)$$

[a] $K_w h^{-1} = [OH^-] \approx 0$.
[b] $Z_{noC} = \sum p c_{pq0}/(b + \sum q c_{pq0})$; $c_{pq0} = \beta_{pq0} h^p b^q$; $B_{noC} \approx B$ and $b \approx B$.

TREATMENT OF DATA

In this study we could not neglect the hydrolysis of Cd(II). We used the equilibrium constants given by Biedermann and Ciavatta [5] (within parentheses is given log β_{pq0}; $\beta_{pq0} = [H_pB_q]h^{-p}b^{-q}$):

$CdOH^+(-10.2 \pm 0.1)$; $Cd_2OH^{3+}(-9.10 \pm 0.05)$; $Cd_4(OH)_4^{4+}(-31.8 \pm 0.1)$ (7)

We first studied the range $-4.5 \leq \log h \leq -1.0$, where we, as a first guess, assumed the complexes to be of the general form B_qC_r (Fig. 1). In the range $-6.5 \leq \log h \leq -4.5$ we also have complexes $H_pB_qC_r$ with $p < 0$, indicated by the fact that $Z^* < 0$, (Fig. 2). At first, the two ranges of log h were treated separately, using normalized curves [6-8] and the MESAK method.[9,10] Data

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$^+$] (≡"LOG A"); H (≡"ATOT") and $(H_{calc}-H)10^3$ (≡"DATOT"). H_{calc} was calculated, using the equilibrium constants in Table 5, for $B=0.4$ M and for $B>0.4$ M the following constants: log $\beta_{\bar{1}10}=4.34$, log $\beta_{011}=0.37$, log $\beta_{\bar{1}21}=-5.48$, log $\beta_{\bar{4}44}=-17.19$, log $\beta_{\bar{5}54}=-23.35$, log $\beta_{\bar{3}33}=-13.91$, log $\beta_{\bar{4}33}=-21.02$. The systematic errors δH and the final values of E_0 are given in Table 1 b.

V	EA(MV)	LOGA	ATOT(MM)	DATOT
SATS 1	V_0 = 30.05			
V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	211.40	-2.222	7.97	0.01
0.940	209.20	-2.259	7.48	-0.00
2.820	204.80	-2.334	6.59	0.01
4.420	200.70	-2.403	5.92	-0.01
5.980	196.40	-2.476	5.31	-0.02
7.600	191.80	-2.554	4.74	-0.01
9.240	186.60	-2.642	4.21	0.00
10.660	181.40	-2.730	3.78	-0.01
12.180	175.30	-2.833	3.36	0.00
13.960	167.00	-2.974	2.90	0.01
15.100	160.40	-3.085	2.62	0.01
15.920	155.20	-3.173	2.43	0.01
17.100	146.90	-3.313	2.17	0.01
18.040	139.80	-3.434	1.97	0.02
19.020	132.30	-3.560	1.77	0.02
20.040	123.80	-3.704	1.57	0.01
21.140	114.90	-3.855	1.37	0.00
22.420	104.80	-4.025	1.14	-0.01
23.540	96.20	-4.171	0.95	-0.01
24.720	84.90	-4.362	0.75	-0.06
SATS 2	V_0 = 30.05			
V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	47.40	-4.990	0.21	-0.05
0.130	52.70	-4.900	0.26	-0.04
0.300	58.50	-4.802	0.31	-0.03
0.500	64.70	-4.697	0.38	-0.02
0.740	70.60	-4.597	0.47	-0.01
0.970	75.90	-4.508	0.54	-0.00
1.220	81.10	-4.420	0.63	0.01
1.480	85.80	-4.340	0.71	0.01
1.760	90.30	-4.264	0.80	0.02
2.050	95.00	-4.185	0.89	0.03
2.350	99.30	-4.112	0.98	0.03
2.700	104.20	-4.029	1.09	0.04
3.050	108.70	-3.953	1.19	0.04
11.490	171.60	-2.890	3.16	0.01
12.490	174.70	-2.837	3.34	0.01
13.550	177.50	-2.790	3.52	0.00
14.620	180.00	-2.747	3.70	0.00
15.750	182.20	-2.710	3.87	-0.01
17.250	184.90	-2.665	4.09	-0.01
18.800	187.30	-2.624	4.31	-0.00
20.680	189.70	-2.583	4.55	-0.00
23.530	192.80	-2.531	4.89	0.00
27.960	196.40	-2.470	5.34	-0.00
32.780	199.30	-2.421	5.77	-0.01
38.640	202.20	-2.371	6.20	0.01
45.390	204.50	-2.332	6.62	-0.00
SATS 3	V_0 = 30.01			
V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	248.30	-1.691	30.32	0.01
1.100	246.10	-1.729	28.62	0.02
2.920	242.30	-1.793	26.04	-0.00
5.340	237.10	-1.882	23.02	0.02
7.220	232.70	-1.957	20.95	0.00
11.900	220.10	-2.171	16.60	0.01
16.020	204.90	-2.429	13.51	-0.01
18.500	192.30	-2.643	11.90	0.01
20.140	181.60	-2.824	10.92	0.03
21.120	174.20	-2.949	10.36	0.04
22.340	164.10	-3.120	9.70	0.03
23.640	153.80	-3.294	9.03	0.01
25.040	144.80	-3.446	8.34	0.06
26.560	135.60	-3.602	7.64	0.03
28.480	126.10	-3.762	6.80	0.03
30.180	118.90	-3.884	6.10	0.03
31.900	112.20	-3.997	5.43	0.03
33.560	105.80	-4.106	4.81	-0.01
36.300	95.80	-4.275	3.87	-0.06
37.980	89.90	-4.374	3.33	-0.06
39.420	84.90	-4.459	2.89	-0.06
41.480	77.30	-4.587	2.29	-0.05
43.280	70.10	-4.709	1.79	-0.05
45.480	60.60	-4.870	1.21	-0.03
47.500	50.50	-5.040	0.71	-0.02
49.080	42.00	-5.184	0.34	0.00
50.280	35.40	-5.296	0.06	0.02
51.500	28.80	-5.407	-0.21	0.03
52.980	21.20	-5.536	-0.52	0.04
54.480	14.80	-5.644	-0.83	0.06
56.040	8.90	-5.744	-1.14	0.05
57.600	4.20	-5.823	-1.44	0.06
59.600	-0.90	-5.909	-1.81	0.05
61.640	-5.20	-5.982	-2.17	0.03
64.740	-10.40	-6.070	-2.69	-0.00
69.120	-16.20	-6.168	-3.37	-0.07
75.120	-22.10	-6.268	-4.20	-0.12
82.140	-27.70	-6.362	-5.07	-0.17
SATS 4	V_0 = 30.01			
V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	262.20	-1.425	57.40	0.14
1.560	258.60	-1.487	52.47	0.04
3.760	253.20	-1.580	46.30	-0.09
5.600	248.60	-1.659	41.72	0.11
7.680	242.40	-1.766	37.09	-0.03
9.960	235.10	-1.890	32.56	0.18
15.650	203.70	-2.424	23.24	0.08
16.400	196.80	-2.541	22.15	0.12
17.070	188.90	-2.674	21.26	0.07
17.960	177.70	-2.864	20.08	0.09
18.860	166.10	-3.060	18.93	0.12
19.820	155.10	-3.246	17.76	0.16
20.780	145.40	-3.410	16.62	0.12
22.040	135.30	-3.581	15.20	0.09
23.540	125.50	-3.747	13.59	0.06
25.120	116.70	-3.895	11.99	0.02
27.120	106.80	-4.063	10.09	-0.03
29.260	97.20	-4.225	8.20	-0.04
31.360	87.90	-4.382	6.47	-0.04
33.260	79.10	-4.531	5.01	-0.03
35.020	70.20	-4.682	3.73	-0.03
36.580	61.60	-4.827	2.65	0.01
38.060	52.20	-4.986	1.67	0.03
39.720	40.10	-5.190	0.63	0.05
41.400	27.90	-5.397	-0.38	0.10
42.880	18.60	-5.554	-1.23	0.12
44.620	10.20	-5.696	-2.19	0.08
46.580	3.30	-5.812	-3.21	-0.06
49.100	-2.70	-5.914	-4.46	-0.20
53.100	-9.60	-6.031	-6.28	-0.37
58.100	-15.70	-6.134	-8.32	-0.32
64.120	-21.90	-6.238	-10.49	-0.24
70.140	-27.70	-6.336	-12.40	-0.22
76.140	-32.80	-6.423	-14.09	-0.09
SATS 5	V_0 = 30.01			
V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	-31.30	-6.459	-15.65	0.85
0.690	-23.60	-6.329	-12.98	0.50
1.300	-17.00	-6.217	-10.71	0.40
1.900	-10.90	-6.114	-8.56	0.31
2.500	-4.90	-6.013	-6.50	0.18
3.100	2.00	-5.896	-4.50	0.12
3.750	12.30	-5.722	-2.43	0.09
4.250	24.50	-5.516	-0.88	-0.01
4.760	42.50	-5.211	0.65	-0.07
5.260	59.90	-4.917	2.11	-0.01
5.760	73.60	-4.686	3.52	0.14
6.310	81.20	-4.557	5.04	-0.30
6.910	90.90	-4.393	6.63	-0.32
7.610	101.30	-4.217	8.44	-0.19
8.510	112.60	-4.026	10.06	-0.17
9.660	127.30	-3.778	13.35	-0.03
10.770	142.10	-3.528	15.60	-0.03
11.870	158.90	-3.243	18.10	-0.17
12.770	176.80	-2.941	19.89	-0.16
13.370	188.50	-2.743	21.05	-0.16
14.020	199.40	-2.558	22.27	-0.11
15.520	215.10	-2.292	24.94	-0.17
19.020	232.90	-1.990	30.54	-0.47
23.540	245.70	-1.771	36.70	0.13
28.520	252.80	-1.650	42.38	-0.06
33.530	257.50	-1.569	47.19	-0.28
SATS 6	V_0 = 30.01			
V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	288.30	-1.098	119.65	-0.13
1.140	285.80	-1.142	111.99	0.01
2.480	282.80	-1.196	103.67	0.03
4.060	279.00	-1.262	94.71	-0.11
6.060	273.90	-1.351	84.48	-0.04
8.220	267.70	-1.459	74.65	0.00
12.020	253.80	-1.698	59.79	0.07
14.860	237.70	-1.973	50.33	-0.02
16.920	217.80	-2.311	44.19	-0.00
17.940	201.80	-2.582	41.34	-0.01
18.760	187.20	-2.829	39.14	0.13
19.440	174.30	-3.048	37.37	-0.00
20.048	165.30	-3.200	35.84	-0.05
20.860	156.90	-3.342	33.82	0.23
21.940	146.20	-3.523	31.25	0.08
23.280	136.20	-3.692	28.21	0.04
24.840	126.30	-3.859	24.86	-0.12
26.740	116.30	-4.028	21.03	-0.14
28.980	105.00	-4.219	16.83	-0.36
31.560	92.90	-4.424	12.36	-0.31
33.860	82.10	-4.607	8.69	-0.02
35.580	73.00	-4.760	6.11	0.18
37.060	63.20	-4.926	4.00	0.16
38.180	55.80	-5.051	2.46	0.32
39.580	42.80	-5.271	0.01	-0.04
41.100	33.10	-5.435	-1.32	-0.02
42.580	26.40	-5.548	-3.12	-0.10
44.620	20.20	-5.653	-5.49	-0.19
48.080	13.30	-5.770	-9.22	-0.18
53.080	6.00	-5.893	-14.06	-0.10
58.100	0.00	-5.994	-18.36	0.09
64.120	-6.80	-6.109	-22.92	0.13
71.120	-14.90	-6.246	-27.54	-0.11
77.120	-21.80	-6.363	-31.02	-0.23
83.140	-28.20	-6.471	-34.14	-0.02
90.160	-34.80	-6.583	-37.38	0.59
SATS 7	V_0 = 30.01			
V	EA(MV)	LOGA	ATOT(MM)	DATOT
0.000	-42.30	-6.387	-31.68	-0.26
0.560	-38.30	-6.320	-29.09	-0.88
1.400	-31.50	-6.205	-25.39	-0.86

Table 1a. Continued.

2.320	-25.10	-6.097	-21.55	-0.76
3.500	-17.90	-5.975	-16.94	-0.55
5.060	-9.30	-5.829	-11.32	-0.32
6.250	-2.30	-5.711	-7.35	-0.06
7.410	7.00	-5.554	-3.73	0.40
8.330	17.80	-5.371	-1.02	0.49
9.140	29.70	-5.170	1.27	0.31
9.820	39.70	-5.001	3.11	0.20
10.510	48.60	-4.851	4.92	0.15
11.320	57.20	-4.705	6.97	0.12
12.690	68.80	-4.509	10.26	0.15
14.080	78.20	-4.350	13.38	0.20
15.680	87.00	-4.202	16.75	0.12
18.090	99.20	-3.995	21.39	0.26
21.510	115.10	-3.726	27.23	0.33
25.040	132.80	-3.427	32.50	0.34
30.050	167.50	-2.840	38.92	0.25
NEW BURET				
0.520	193.40	-2.402	43.08	0.03
1.130	212.20	-2.083	47.86	-0.01
2.480	232.50	-1.737	58.11	0.04
4.630	247.80	-1.474	73.56	-0.06
6.540	255.90	-1.333	86.45	-0.07
9.050	263.20	-1.205	102.30	0.01
11.570	268.50	-1.111	117.10	0.29
15.030	273.70	-1.018	135.80	0.14
SATS 8	Vo = 30.01			
V	EA(MV)	LOGA	ATOT(MM)	$DATOT$
2.300	298.70	-0.916	202.22	-0.84
4.200	293.80	-1.005	178.64	-0.05
6.380	287.10	-1.125	155.03	-0.15
8.820	277.90	-1.287	131.55	-0.09
9.820	273.20	-1.369	122.76	-0.20
10.940	266.90	-1.479	113.42	-0.41
12.440	254.70	-1.688	100.04	0.11
14.000	238.70	-1.962	90.33	-0.04
15.000	216.00	-2.347	83.47	-0.49
16.020	183.00	-2.986	76.78	-0.76
17.020	162.80	-3.248	70.49	-0.54
18.040	146.70	-3.486	64.36	-0.74
19.440	135.60	-3.708	56.35	-0.52
21.540	120.60	-3.961	45.14	-0.15
24.040	105.20	-4.222	32.94	0.12
26.560	87.90	-4.514	21.74	-0.82
28.860	71.10	-4.798	12.35	-0.56
31.060	51.40	-5.131	4.02	-0.31
32.080	43.60	-5.263	0.37	-0.23
34.060	34.20	-5.422	-6.40	-0.05
36.060	28.70	-5.515	-12.83	0.71
39.080	22.00	-5.628	-21.82	1.22
43.080	14.70	-5.751	-32.59	1.87
46.080	9.10	-5.846	-39.93	1.58
50.060	1.70	-5.971	-48.81	1.17
54.080	-6.80	-6.115	-56.93	0.04
57.080	-13.20	-6.223	-62.50	-0.34
60.100	-20.30	-6.343	-67.73	-0.80
63.100	-26.70	-6.451	-72.59	-0.38
66.100	-33.10	-6.560	-77.15	0.29
69.120	-39.10	-6.661	-81.46	1.36
SATS 9	Vo = 40.85			
V	EA(MV)	LOGA	ATOT(MM)	$DATOT$
0,235	73,70	-4,644	0.32	-0.05
0,513	79,20	-4,551	0.40	-0.05
0,885	85,90	-4,438	0.48	-0.02
1,100	90,70	-4,356	0.56	-0.02
1,455	96,10	-4,265	0.66	-0.01
1,851	101,50	-4,174	0.76	-0.00
2,243	106,50	-4,089	0.87	0.00
2,683	111,60	-4,003	0.98	0.01
3,098	115,80	-3,932	1.09	0.01
3,693	121,70	-3,832	1.23	0.01
4,373	128,00	-3,726	1.40	0.01
5,090	134,00	-3,624	1.56	-0.00
5,890	142,10	-3,487	1.74	0.04
6,690	148,00	-3,388	1.92	0.03
7,490	153,30	-3,298	2.09	0.03
8,380	158,60	-3,208	2.27	0.02
9,430	164,10	-3,115	2.47	0.02
10,720	169,60	-3,022	2.71	0.01
12,150	174,80	-2,934	2.97	0.01
13,620	179,10	-2,862	3.21	-0.00
15,320	183,20	-2,792	3.48	-0.01
17,280	187,20	-2,725	3.77	-0.01
19,590	190,90	-2,662	4.09	-0.02
22,560	194,90	-2,594	4.47	-0.01
25,950	198,60	-2,532	4.85	0.01
30,130	201,90	-2,476	5.28	-0.01
36,140	205,80	-2,410	5.81	0.02
44,140	209,20	-2,352	6.41	-0.01
SATS10	Vo = 30.01			
V	EA(MV)	LOGA	ATOT(MM)	$DATOT$
0,000	270,50	-1,391	60,39	0.18
3,900	261,60	-1,545	48,38	0.03
5,500	257,40	-1,617	44,22	-0.19
6,660	254,40	-1,669	41,43	-0.11
8,020	250,60	-1,734	38,37	-0.06
10,520	242,70	-1,869	33,29	0.05
15,500	218,80	-2,275	24,83	0.02
17,460	202,50	-2,552	21,99	-0.01
18,580	190,20	-2,760	20,47	-0.03
19,480	179,60	-2,939	19,30	-0.04
21,700	158,80	-3,291	16,58	0.13
23,240	146,50	-3,499	14,83	-0.01
24,500	138,90	-3,627	13,47	0.01
26,100	130,30	-3,773	11,83	0.01
28,160	120,60	-3,937	9,85	0.03
30,460	110,70	-4,104	7,80	0.12
33,440	97,30	-4,331	5,37	0.07
36,000	84,90	-4,540	3,45	0.06
38,520	71,10	-4,774	1,71	0.08
40,000	62,20	-4,924	0,74	0.09
41,740	51,10	-5,112	-0,34	0.06
43,280	41,90	-5,267	-1,26	0.02
44,780	34,60	-5,391	-2.12	0.02
46,800	26,30	-5,531	-3,22	-0.04
49,080	19,20	-5,651	-4,40	-0.10
51,680	13,10	-5,754	-5,66	-0.16
54,820	7,70	-5,845	-7,08	-0.11
58,760	2,20	-5,938	-8,72	-0.06
64,640	-4,90	-6,058	-10,91	-0.07
70,660	-10,90	-6,160	-12,89	0.03
SATS11	Vo = [illegible]			
V	EA(MV)	LOGA	ATOT(MM)	$DATOT$
0,000	272,80	-1,457	75,70	-0.91
6,020	245,30	-1,928	51,61	-0.22
9,020	210,60	-2,517	41,91	-0.39
10,540	183,00	-2,985	37,46	-0.56
12,180	162,60	-3,330	32,95	-0.61
13,640	149,60	-3,549	29,18	-0.79
15,540	136,80	-3,766	24,58	-0.85
18,040	123,00	-3,999	19,01	-0.74
20,560	110,00	-4,219	13,87	-0.60
23,060	97,20	-4,435	9,19	-0.25
25,060	86,20	-4,621	5,71	0.13
26,280	77,80	-4,763	3,70	0.12
27,580	68,50	-4,920	1,63	0.19
28,880	59,30	-5,076	-0,35	0.30
30,080	48,80	-5,253	-2,12	-0.26
31,580	41,20	-5,382	-4,24	-0.26
33,580	36,00	-5,470	-6,92	0.57
37,080	27,90	-5,607	-11,28	1.09
42,080	18,80	-5,761	-16,85	1.12
48,080	9,00	-5,926	-22,67	0.47
54,100	0,70	-6,067	-27,76	0.41
60,100	-7,90	-6,212	-32,20	0.15
64,120	-13,80	-6,312	-34,89	0.07
68,120	-19,10	-6,401	-37,36	0.29
70,120	-21,60	-6,444	-38,53	0.47
74,140	-26,10	-6,520	-40,75	1.03
SATS12	Vo = 30.01			
V	EA(MV)	LOGA	ATOT(MM)	$DATOT$
0,000	291,60	-1,283	71,82	0.25
0,800	289,70	-1,316	68,45	-0.22
2,200	286,90	-1,365	62,95	-0.14
3,600	283,60	-1,422	57,90	-0.16
4,600	281,30	-1,462	54,55	-0.13
5,700	278,70	-1,507	51,08	-0.06
6,700	276,30	-1,548	48,10	0.08
7,800	273,30	-1,600	45,01	-0.02
14,020	252,00	-1,964	30,44	0.12
18,030	226,40	-2,399	23,04	0.13
20,040	205,10	-2,760	19,78	0.17
21,540	187,70	-3,054	17,52	0.11
23,240	171,70	-3,325	15,10	0.03
25,050	157,90	-3,558	12,69	-0.12
27,050	145,10	-3,774	10,21	-0.25
29,560	131,30	-4,008	7,33	-0.16
31,760	118,90	-4,217	5,00	-0.09
33,660	106,70	-4,424	3,11	-0.10
35,470	94,40	-4,631	1,42	-0.03
37,170	81,80	-4,844	-0,09	-0.01
38,380	72,80	-4,997	-1,12	-0.06
39,780	63,60	-5,152	-2,26	-0.11
41,780	53,30	-5,326	-3,82	-0.10
43,950	44,80	-5,470	-5,41	-0.03
46,600	36,60	-5,609	-7,23	0.07
49,890	28,40	-5,747	-9,33	0.16
53,960	19,90	-5,891	-11,70	0.20
58,880	10,90	-6,043	-14,27	0.15
64,060	2,30	-6,188	-16,68	0.06
68,700	-4,80	-6,308	-18,63	-0.02
73,420	-10,10	-6,398	-20,44	0.29
75,540	-14,20	-6,467	-21,19	-0.12
81.150	-20,70	-6,577	-23,06	-0.16
SATS13	Vo = [illegible]			
V	EA(MV)	LOGA	ATOT(MM)	$DATOT$
0,000	6,80	-6,081	-70,83	-0.87
0,400	12,20	-5,989	-66,46	-0.65
0,810	17,30	-5,903	-62,10	-0.19
1,400	23,90	-5,792	-56,03	0.74
2,250	30,80	-5,675	-47,68	0.59
3,150	37,70	-5,558	-39,30	1.13
4,050	43,90	-5,453	-31,36	1.39
5,010	50,10	-5,349	-23,34	1.10
6,010	57,20	-5,229	-15,44	0.73
7,110	67,90	-5,048	-7,25	0.72
8,260	81,80	-4,813	0,82	-0.01
9,010	91,90	-4,642	5,82	-0.21
9,770	101,20	-4,485	10,70	-0.37
10,670	111,00	-4,319	16,24	-0.29
11,770	120,70	-4,155	22,69	-0.37
13,020	130,20	-3,995	29,61	-0.33
14,530	140,00	-3,829	37,46	-0.47
16,530	152,20	-3,623	47,07	-0.41
18,780	166,20	-3,386	56,94	-0.14
21,040	181,90	-3,120	65,98	-0.05
24,050	211,80	-2,614	76,85	0.25
25,320	226,70	-2,362	81,08	0.15
28,320	251,30	-1,944	90,34	-0.19
32,070	267,00	-1,676	100,65	-0.23
35,880	275,90	-1,523	109,93	-0.39
38,090	279,70	-1,457	114,84	-0.34

Table 1a. Continued.

40,590	283,10	-1,398	120,02	-0.39
43,600	286,50	-1,339	125,79	-0.28
47,100	289,70	-1,283	131,93	-0.08
50,100	291,80	-1,247	136,77	-0.28
54,210	294,40	-1,201	142,84	-0.02
58,820	296,70	-1,160	148,98	0.06
64,120	298,70	-1,125	155,29	-0.34
SAT814	V_0=30.00			
V	EA(MV)	LOGA	ATOT(MM)	DATOT
0,000	317,70	-0,791	241,33	0.36
1,530	314,70	-0,847	222,56	-0.58
2,550	312,80	-0,883	211,03	-0.15
3,450	311,00	-0,916	201,44	-0.21
4,350	309,20	-0,949	192,35	-0.00
5,400	307,10	-0,987	182,33	0.53
7,020	303,20	-1,058	167,98	-0.56
8,250	300,20	-1,111	157,90	-0.58
9,450	297,10	-1,166	148,67	-0.69
10,950	292,90	-1,240	137,90	-0.66
13,500	284,20	-1,392	121,29	-1.13
16,830	268,90	-1,656	102,31	-0.94

19,530	245,80	-2,050	88,80	-1.60
21,330	220,70	-2,476	80,59	-1.63
22,830	200,60	-2,817	74,17	-1.64
24,930	182,80	-3,118	65,77	-1.18
27,960	165,70	-3,407	54,72	-0.76
30,960	153,20	-3,618	44,87	-0.33
36,060	134,30	-3,938	30,17	-0.66
40,560	118,80	-4,200	18,96	-0.57
45,090	101,70	-4,489	9,04	-0.65
49,590	84,70	-4,776	0,30	-0.30
54,090	71,20	-5,005	-7,51	0.30
57,770	64,00	-5,126	-13,30	1.12
62,120	57,10	-5,243	-19,54	1.25
68,120	51,10	-5,344	-27,25	2.41
72,150	47,20	-5,410	-31,92	2.33
NEW BURET				
2,250	43,70	-5,469	-35,48	2.43
6,750	37,10	-5,581	-45,04	2.45
18,030	18,90	-5,889	-63,68	0.29
33,060	-5,00	-6,293	-83,69	1.49

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 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)	$10^3(\delta H \pm 3\sigma)$	
1	0.4	0.002	0.00797	−0.00801	342.9	[a] 342.9±0.2	[a] −0.01±0.01	[b] −0.01±0.02
2	0.4	0.002	0.00023	0.01088	342.4	342.6±0.3	−0.02±0.02	−0.03±0.02
3	0.4	0.010	0.03032	−0.01800	348.7	348.6±0.2	0.02±0.04	−0.01±0.07
4	0.4	0.020	0.05736	−0.0423	347.2	347.1±0.2	±0.0 ±0.1	−0.1 ±0.2
5	0.4	0.020	−0.01579	0.1033	350.7	350.8±0.8	0.2 ±0.3	±0.0 ±0.2
6	0.4	0.040	0.1195	−0.0898	354.7	354.6±0.2	0.2 ±0.2	−0.1 ±0.3
7	0.4	0.040	−0.0317	0.1094	335.6	335.6±0.3	−0.3 ±0.4	−0.2 ±0.5
8	0.4	0.080	0.2345	−0.2186	354.8	355.0±0.4	−0.1 ±0.6	−0.5 ±0.5
9	0.7	0.002	0.00025	0.01210	348.4	[b] 348.4±0.3	[b] 0.05±0.02	
10	0.7	0.020	0.06040	−0.04400	353.5	353.4±0.2	−0.1 ±0.1	
11	0.7	0.040	0.0755	−0.1006	358.7	359.5±1.5	0.2 ±0.7	
12	1.2	0.020	0.07185	−0.05812	368.4	368.4±0.2	±0.0 ±0.2	
13	1.2	0.080	−0.0709	0.2611	366.5	366.4±0.4	−0.1 ±0.6	
14	1.4	0.080	0.2406	−0.1463	367.4	367.2±0.4	0.7 ±1.0	

[a] Values obtained, using data with $B=0.4$ M and the constants in Table 5.
[b] Values from calculations, using all data giving also $\log \beta_{\bar{1}01}=4.34$, $\log \beta_{011}=0.37$, $\log \beta_{\bar{1}21}= -5.48$, $\log \beta_{\bar{4}44}= -17.19$, $\log \beta_{\bar{5}54}= -23.35$, $\log \beta_{\bar{3}33}= -13.91$, and $\log \beta_{\bar{4}33}= -21.02$. For $B=0.4$ M, E_0 differed only ≤ 0.1 mV from those given under *a*.

from the two ranges were then treated together by the least squares program LETAGROP,[11,12] using the primary data $(V,E)_{B,C}$ directly, minimizing $\sum(Z_{calc}-Z)^2$ (*cf.* eqns. (2)−(5)).

Graphical treatment of data in the range $-4.5 \leq \log h \leq -1.0$

$Z^*(\log h)_{B,C}$ for different C-values coincide, as long as B is constant. The shape of $Z^*(\log h)_{B,C}$ is the same as for a monobasic acid. Curves for different B-values are approximately parallel for $\log h < -3.5$ (Fig. 1).

1. *The values of r indicated by the curves* $Z^*(\log h)_{B,C}$. We make use of the self medium and consider first each B-value separately, writing the complexes formally H_pC_r. From eqn. (6) in this article and eqns. (4), (5 a), (7 a), (7 c) and (8 a) in part II [2] we obtain

$$Z^* = \sum_{r\neq 0} p\beta_{pqr}h^pb^qc^r/(c + \sum_{r\neq 0} r\beta_{pqr}h^pb^qc^r) \quad (8\text{ a})$$

Z^* is independent of C only if $r=1$ (if c cannot be neglected). As seen in Fig. 1, $Z^*(\log h)_{B,C}$ for different C-values gives a single curve indicating that $r=1$ for the main complexes.

2. *The values of q. Normalized curves fitted to* $Z^*(\log h)_{B,C}$. *Determination of* β_{pqr}. If we assume cadmium complexes of the form B_qC_r ($p=0$) and use the information that $r=1$ we get

$$Z^* = [H_2Asc]/([H_2Asc]+[HAsc^-]+CdHAsc^+ + Cd_2HAsc^{3+}+\cdots) \quad (8\text{ b})$$

Eqn. (8 b) can be written

$$Z^* = \beta_{101}h/(1+B\,F(B)+\beta_{101}h);\;\; F(B)=\sum_q \beta_{0q1}B^{q-1} \quad (8\text{ c})$$

Eqn. (8 c) can be normalized to

$$Z^* = V/(1+V),\text{ where } V=[\beta_{101}/(1+B\,F(B))]h \quad (8\text{ d})$$

The normalized function $[V/(1+V)](\log V)$ could be fitted to the experimental curves $Z^*(\log h)_{B,C}$ (Fig. 1). From the translation $\log V - \log h = \log [\beta_{101}/(1+B\,F(B)]$ of each curve in Fig. 1 to the "best" fit we calculated $F(B)$ using $\log \beta_{101} = 4.360$:

$F(B) = 0.41 \pm 0.05$ independent of B, thus $q=1$ (*cf.* (8 c)). The predominating complex is $CdHAsc^+$ with

$$\log \beta_{011} = 0.41 \pm 0.05 \quad (8\text{ e})$$

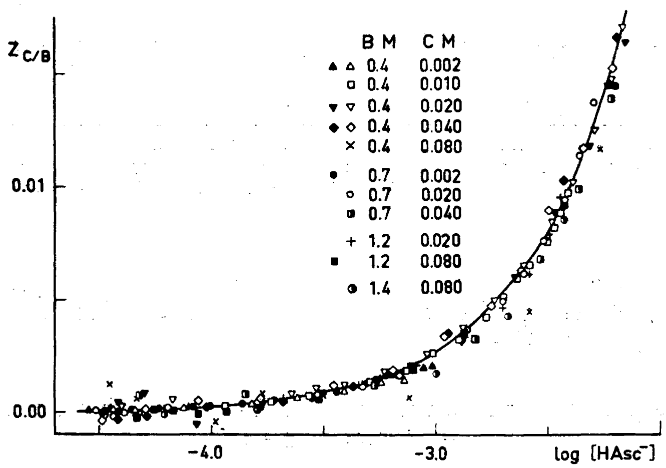

Fig. 3. $Z_{C/B}$ (= the average number of C bound per B) as a function of $c=[HAsc^-]$. The full curve is the normalized function $[x/(1+x)](\log x)$ corresponding to $\log \beta_{011} = 0.40$. Filled symbols represent back titrations.

3. *The value of q, r and* β_{pqr} *obtained using* $Z_{C/B}$ *(log c)*$_{B,C}$. It is possible to calculate $Z_{C/B}$ and $c = [\text{HAsc}^-]$ if we assume B_qC_r complexes only, *i.e.* $p=0$. The average number of H^+ bound per C in the complexes $= Z'_{H/C}$ is then zero. From eqns. (12) and (9 a) in part II [2] we can calculate Z_{noB} and C_{noB} ($B_{\text{noC}}Z_{\text{noC}}=0$). $Z_{C/B}$ can then be obtained from eqn. (9 c), and c from eqn. (5 a).

In Fig. 3 can be seen that $Z_{C/B}$ $(\log[\text{HAsc}^-])_{B,C}$ coincide for different values of B indicating that $q=1$.

If we assume that CdHAsc^+ is the only complex, then:

$$Z_{C/B} = \beta_{011}c/(1+\beta_{011}c),\ c = [\text{HAsc}^-] \tag{8 f}$$

The experimental points could be fitted with the normalized function $[x/(1+x)](\log x)$, $x = \beta_{101}c$ (Fig. 3) giving:

$$\log \beta_{011} = 0.40 \pm 0.05 \tag{8 g}$$

Graphical treatment of data in the range $-6.5 \leq \log h \leq -4.5$

In Fig. 2 are shown the data for $B = 0.4$ M. The complexes can formally be written H_pC_r (B in the medium).[2] The curves for different C-values coincide for $\log h > -5.2$. This indicates $r=1$.

We applied the MESAK [9,10] method (Figs. 4 a and b). This indicated that complexes with $p=-1$, and $r=1$ predominate for $\log h > -5.4$, that is Cd_QAsc. For $\log h < -5.4$ complexes with higher q- and r-values also seem to be present.

For $\log h > -5.4$ we assumed one complex with $p=-1$, and $r=1$, thus Cd_QAsc. The value of Q can be determined from a comparison between different media (*cf.* part II [2]).

1. Use of normalized functions to determine Q and $\beta_{\bar{1}Q1}$ *for* Cd_QAsc *(Fig. 5).* Assuming one basic complex Cd_QAsc, we obtain:

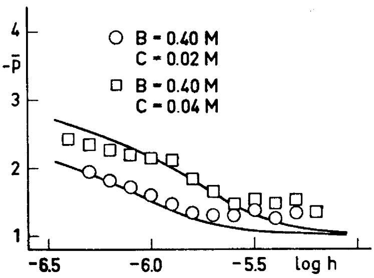

Fig. 4 a. $\bar{p}$ (= the average number of H^+ bound per complex excluding CdHAsc^+) as a function of $\log h$. Experimental values obtained by the MESAK [9] method are marked with ○ and □. Theoretical values, calculated by HALTAFALL,[14] are represented by solid curves (equilibrium constants from Table 5).

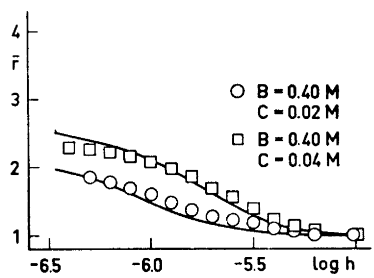

Fig. 4 b. $\bar{r}$ (= the average number of HAsc^- bound per complex excluding CdHAsc^+) as a function of $\log h$. Experimental values obtained by the MESAK [9] method are marked with ○ and □. Theoretical values, calculated by HALTAFALL,[14] are represented by solid curves (equilibrium constants from Table 5).

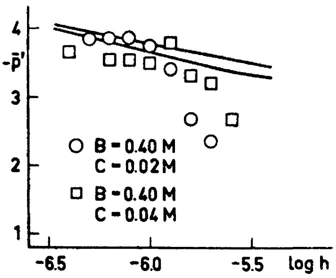

Fig. 4 c. $\bar{p}'$ (= the average number of H^+ bound per complex, excluding $CdHAsc^+$ and Cd_2Asc^{2+}) as a function of log h. Experimental values obtained by the MESAK [9] method are marked with ○ and □. Theoretical values, calculated by HALTAFALL,[14] are represented by solid lines (equilibrium constants from Table 5).

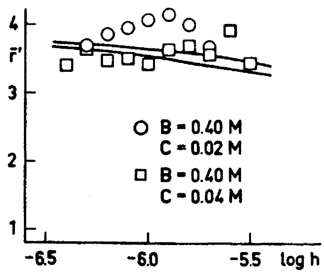

Fig. 4 d. $\bar{r}'$ (= the average number of $HAsc^-$ bound per complex, excluding $CdHAsc^+$ and Cd_2Asc^{2+}) as a function of log h. Experimental values obtained by the MESAK [9] method are marked with ○ and □. Theoretical values, calculated by HALTAFALL,[14] are represented by solid lines (equilibrium constants from Table 5).

$$Z^* = ([H_2Asc] - [Cd_QAsc])/([H_2Asc] + [HAsc^-] + [CdHAsc^+] + [Cd_QAsc]) \quad (9\text{ a})$$

which can be written

$$Z^* = (\beta_{101}h - \beta_{\bar{1}Q1}B^Q\ h^{-1})/(1 + \beta_{101}h + \beta_{011}B\ + \beta_{\bar{1}Q1}B^Q\ h^{-1}) \quad (9\text{ b})$$

Eqn. (9 b) can be normalized to

$$Z^* = (V - RV^{-1})/(1 + V + RV^{-1});\ V = [\beta_{101}/(1 + B\ \beta_{011})]h$$

$$R = \beta_{101}\beta_{\bar{1}Q1}B^Q/(1 + B\beta_{011})^2 \quad (9\text{ c})$$

The normalized function $[(V - RV^{-1})/(1 + V + RV^{-1})](\log V)$ was fitted to the curves in Fig. 5. From the "best" fit we got values of R, using $\log \beta_{011} = 0.41$,

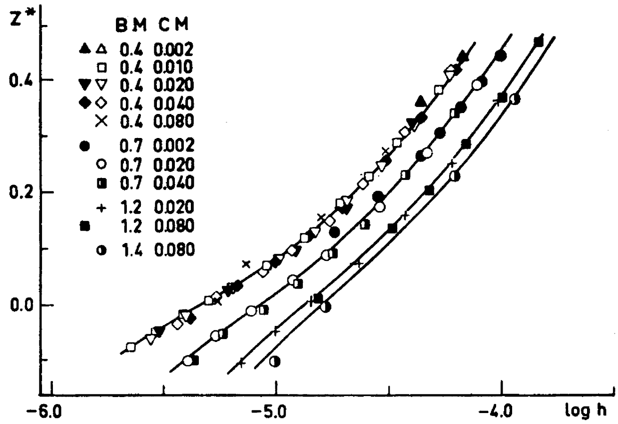

Fig. 5. Z^* (= the average number of H^+ bound per C) as a function of log h. The solid curves are normalized functions $[(V - RV^{-1})/(1 + V + RV^{-1})]$ (log V), corresponding to $\log \beta_{\bar{1}21} = -5.44$.

and log $\beta_{101} = 4.36$. From R, log $\beta_{\bar{1}11}$ or log $\beta_{\bar{1}21}$ were calculated, thus assuming $Q = 1$ or 2 (Table 2). Since $\beta_{\bar{1}21}$ is independent of B, the data are best described by ($\bar{1}21$) with the formation constant

$$\log \beta_{\bar{1}21} = -5.44 \pm 0.10 \qquad (9\text{ d})$$

2. Average composition of complexes $H_pB_qC_r$ *with higher values of* p, q *and* r. The average values of p and r in Figs. 4 a and b, obtained by the MESAK [9,10] method, indicate that at least one more complex with $r > 1$ is present in the solution. This is also indicated by the fact that the curves in Fig. 2 do not coincide.

Table 2. Values of the shape parameter R and the formation constants $\beta_{\bar{1}11}$ and $\beta_{\bar{1}21}$ calculated assuming one complex Cd_QAsc with $p < 0$ to be present, using log $\beta_{011} = 0.41$, and log $\beta_{101} = 4.36$.

B	R	log $\beta_{\bar{1}11}$	log $\beta_{\bar{1}21}$
0.4 M	0.003	-5.8_7	-5.4_7
0.7 M	0.005	-5.6_3	-5.4_8
1.2 M	0.007	-5.3_7	-5.4_5
1.4 M	0.008	-5.2_1	-5.3_6

We calculated new values of $\bar{p}$ and $\bar{r}$, now with Cd_2Asc^{2+} subtracted. As seen in Figs. 4 c and d, these values indicate complexes with $r = 3$ or 4 and, roughly, $-p = r$.

Selection of a set of complexes, giving the best fit with the data by LETAGROP calculations

The data for $B = 0.4$ M were used to select a set of complexes giving "best" fit with these data, choosing $q = r$, since q cannot be determined, while B is kept constant (*cf.* note on the Self medium method in part II [2]). We tried various combinations, starting with (101) + (011) + ($\bar{1}21$) + ($\bar{3}33$). Low values of U and $\sigma(Z)$ were obtained for combinations:

$$(101) + (011) + (\bar{1}21) + (\bar{4}Q_1 4) + \text{a more basic complex } (P_2Q_2R_2) \qquad (10\text{ a})$$

We determined Q_1, P_2, Q_2 and R_2 by calculations on each medium separately, combined with comparisons of log β_{pqr}-values obtained from the different media. As seen in Table 3, the lowest U- and $\sigma(Z)$-values and the best constancy of log $\beta_{\bar{4}Q_14}$ and log $\beta_{P_2Q_2R_2}$ were obtained by (10 b):

$$(101) + (011) + (\bar{1}21) + (\bar{4}44) + (\bar{5}54) \qquad (10\text{ b})$$

We added ($\bar{3}33$) and ($\bar{4}33$) as given in part III [3] of this series. U and $\sigma(Z)$ came out slightly lower than for (10 b). The same values of $\beta_{\bar{4}44}$ and $\beta_{\bar{5}54}$ were obtained within 3σ (Tables 3 and 5). Thus by adding ($\bar{3}33$) and ($\bar{4}33$) we get:

$$(101) + (011) + (\bar{1}21) + (\bar{3}33) + (\bar{4}33) + (\bar{4}44) + (\bar{5}54) \qquad (10\text{ c})$$

From the medium with $B = 0.4$ M we have chosen 121 points and used the "SPECIES SELECTOR" in LETAGROP [13] to systematically try adding new

Table 3. LETAGROP[11,12] calculations minimizing $U_z = \sum (Z_{calc} - Z)^2$. Log $\beta_{101} = 4.37$, log $\beta_{011} = 0.41$, log $\beta_{\bar{1}21} = -5.46$, log $\beta_{\bar{1}10} = -10.2$, log $\beta_{\bar{1}20} = -9.1$, and log $\beta_{\bar{4}44} = -31.8$ were not varied. For the last two columns we use log β_{PQR} = log β_{PR}† − Q log B. See Ref. 2, note on the Self medium method. For example, log $\beta_{\bar{5}54}$ = log $\beta_{\bar{5}44}$ + (5 − 4) log B.

B	Number of points	$U \times 10^4$	(σZ)	log $\beta_{\bar{4}44} \pm 3\sigma$	(log $\beta_{PQR} \pm 3\sigma$)	(PQR)	log β_{PQR} + log B	log β_{PQR} − log B
0.4	239	307	0.0114	−17.14 ± 0.07	−16.54 ± 0.09	($\bar{3}22$)	−16.14	−16.94
		222	0.0097	−17.04 ± 0.05	−23.26 ± 0.07	($\bar{4}22$)	−22.86	−23.66
		228	0.0099	−17.16 ± 0.07	−20.16 ± 0.09	($\bar{4}33$)	−19.76	−20.56
		205	0.0093	−17.02 ± 0.05	−26.93 ± 0.07	($\bar{5}33$)	−26.53	−27.33
		203	0.0093	−17.12 ± 0.07	−23.78 ± 0.06	($\bar{5}44$)	−23.38	−24.18
		214	0.0095	−17.01 ± 0.05	−30.61 ± 0.08	($\bar{6}44$)	−30.21	−31.01
		216	0.0096	−17.13 ± 0.09	−27.48 ± 0.09	($\bar{6}55$)	−27.08	−27.88
		231	0.0099	−17.00 ± 0.05	−34.30 ± 0.09	($\bar{7}55$)	−33.90	−34.70
0.7	84	87	0.0106	−16.75 ± 0.09	−22.81 ± 0.09	($\bar{4}22$)	−22.66	−22.96
		83	0.0101	−16.75 ± 0.09	−26.38 ± 0.08	($\bar{5}33$)	−26.23	−26.53
		86	0.103	−16.96 ± 0.14	−23.25 ± 0.09	($\bar{5}44$)	−23.10	−23.38
		77	0.0097	−16.75 ± 0.08	−29.94 ± 0.09	($\bar{6}44$)	−29.79	−30.09
		99	0.0117	−17.11 ± 0.16	−26.93 ± 0.08	($\bar{6}55$)	−26.78	−27.08
1.2	66	59	0.0097	−16.80 ± 0.07	−23.19 ± 0.14	($\bar{4}22$)	−23.27	−23.11
		52	0.0091	−16.81 ± 0.07	−26.60 ± 0.15	($\bar{5}33$)	−26.68	−26.52
		21	0.0056	−17.00 ± 0.07	−23.30 ± 0.07	($\bar{5}44$)	−23.38	−23.22
		41	0.0080	−16.84 ± 0.07	−30.00 ± 0.12	($\bar{6}44$)	−30.08	−29.92
		36	0.0075	−17.01 ± 0.11	−26.90 ± 0.10	($\bar{6}55$)	−26.98	−26.82
1.4	31	74	0.0203	−16.91 ± 0.14	−22.71 ± 0.3	($\bar{4}22$)	−22.9	−22.6
		12	0.0071	−16.83 ± 0.06	−25.95 ± 0.09	($\bar{5}33$)	−26.10	−25.80
		11	0.0069	−16.96 ± 0.06	−23.01 ± 0.09	($\bar{5}44$)	−23.16	−22.86
		12	0.0071	−16.83 ± 0.06	−29.59 ± 0.10	($\bar{6}44$)	−29.74	−29.44
		18	0.0079	−16.96 ± 0.12	−26.65 ± 0.13	($\bar{6}55$)	−26.79	−26.50

complexes to the model (10 b). None of these could significantly improve the fit* (Fig. 6).

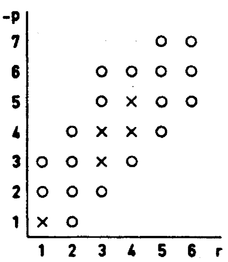

Fig. 6. Complexes tested, using 121 points for $B = 0.4$ M. (p,r) for complexes found in the final model are marked with ×.

One may notice that the average values of p and r for $H_pB_qC_r$ with $p > 1$ in the final model (10 b) agree well with those found by graphical integration

* Those with $\beta_{pqr} < 3\sigma(\beta_{pqr})$ were rejected.

Table 4. LETAGROP calculations minimizing $U_z = \sum(Z_{calc} - Z)^2$. log $\beta_{101} = 4.372$, log $\beta_{011} = 0.41$, log $\beta_{\bar{3}33} = -13.70$, log $\beta_{\bar{4}33} = -21.00$, log $\beta_{\bar{1}10} = -10.2$, log $\beta_{\bar{1}20} = -9.1$, and log $\beta_{\bar{4}40} = -31.8$ were not varied. $\delta E_0 = 0$, and $\delta H = 0$. (Comparison between different media).

B	Number of points	$U_z \times 10^4$	$\sigma(Z)$	log ($\beta_{pqr} \pm 3\sigma$)	(pqr)				
0.4	239	201	0.0093	-5.51 ± 0.04	($\bar{1}21$)	-17.13 ± 0.15	($\bar{4}44$)	-23.34 ± 0.09	($\bar{5}54$)
0.7	84	86	0.0103	-5.48 ± 0.05	($\bar{1}21$)	-16.95 ± 0.19	($\bar{4}44$)	-23.06 ± 0.09	($\bar{5}54$)
1.2	66	18	0.0054	-5.47 ± 0.02	($\bar{1}21$)	-17.03 ± 0.06	($\bar{4}44$)	-23.32 ± 0.06	($\bar{5}54$)
1.4	31	11	0.0069	-5.43 ± 0.06	($\bar{1}21$)	-17.04 ± 0.17	($\bar{4}44$)	-23.11 ± 0.11	($\bar{5}54$)

Table 5. Results of LETAGROP calculations, using 239 points with $B = 0.4$ M, minimizing $U_z = \sum(Z_{calc} - Z)^2$. The corresponding reactions are given in eqn. (12). log $\beta_{\bar{1}10} = -10.2$, log $\beta_{\bar{1}20} = -9.1$, and log $\beta_{\bar{4}40} = -31.8$ were not varied. (Refinement).

		log ($\beta_{pqr} \pm 3\sigma$)						
$U_z \times 10^4$	$\sigma(Z)$	(101)	(011)	($\bar{1}21$)	($\bar{4}44$)	($\bar{5}54$)	($\bar{3}33$)	($\bar{4}33$)
201	0.0093	4.37 ± 0.02	0.41 ± 0.03	-5.52 ± 0.04	-17.16 ± 0.12	-23.36 ± 0.03	-13.71 ± 0.01	-21.02 ± 0.10
						$\delta E_0 = 0$ and $\delta H = 0$		
169	0.0085	4.37 ± 0.02	0.41 ± 0.04	-5.52 ± 0.04	-17.16 ± 0.08	-23.39 ± 0.16	-13.75 ± 0.12	-21.01 ± 0.02
						δE_0 and δH varied (Table 1 b)		

using the MESAK method (Fig. 4). The consistency of the equilibrium constants was checked by calculations on each medium separately (Table 4). The agreement of log β_{pqr} was within 0.15.

Refinement of the equilibrium model by least squares treatment, using LETAGROP

All 239 points from the medium with $B = 0.4$ M were used to refine the equilibrium model (10 c) minimizing $U_z = \sum(Z_{calc} - Z)^2$ (Table 5). Systematic errors were treated as parameters. We assumed analytical errors in $H = \delta H$, and also small errors in $E_0 = \delta E_0$:

Final $H = H$ (calculated from analyses, *cf.* part II [2]) + δH
Final $E_0 = E_0$ (calculated from a few acid points, *cf.* part II [2]) + δE_0 (11)

As seen in Table 1 b, δH and δE_0 are small. The corresponding errors $\delta(\log h)$ and $\delta(Z)$ have no trends. They correspond to very small shifts of the curves $Z(\log h)_{B,C}$ in Figs. 1 and 2. The value of $\sigma(Z) = 0.0085$ is very good.

We also refined the final equilibrium model, using all 420 experimental points from all B-values, treating the systematic errors as parameters. The values of the equilibrium constants were the same (within 3σ) as obtained from the refinement with data for $B = 0.4$ M, but $\sigma(Z) = 0.0098$ was somewhat higher. A small variation in the activity coefficients may cause the higher $\sigma(Z)$ when all data were used. Analytical errors in H, B or C, or small amounts of another complex could also give a higher $\sigma(Z)$.

To estimate the systematic errors we practised the same strategy as in parts I [1] and III.[3]

RESULT AND DISCUSSION

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

	pqr	Reaction	$\log(\beta_{pqr} \pm 3\sigma)$	
1.	101	$HAsc^- + H^+ \rightleftharpoons H_2Asc$	4.37 ± 0.02	
2.	011	$Cd^{2+} + HAsc^- \rightleftharpoons CdHAsc^+$	0.42 ± 0.04	
3.	$\bar{1}21$	$2\,Cd^{2+} + HAsc^- \rightleftharpoons Cd_2Asc^{2+} + H^+$	-5.52 ± 0.04	(12)
4.	$\bar{4}44$	$4\,Cd^{2+} + 4\,HAsc^- \rightleftharpoons Cd_4Asc_4 + 4\,H^+$	-17.16 ± 0.08	
5.	$\bar{5}54$	$5\,Cd^{2+} + 4\,HAsc^- \rightleftharpoons Cd_5Asc_4OH^+ + 5\,H^+$	-23.39 ± 0.16	

We have also found evidence for Cd_3Asc_3 and $Cd_3Asc_3OH^-$ (*cf.* part III [3]):

	pqr	Reaction	$\log(\beta_{pqr} \pm 3\sigma)$
6.	$\bar{3}33$	$3\,Cd^{2+} + 3\,HAsc^- \rightleftharpoons Cd_3Asc_3 + 3\,H^+$	-13.75 ± 0.12
7.	$\bar{4}33$	$3\,Cd^{2+} + 3\,HAsc^- \rightleftharpoons Cd_3Asc_3OH^- + 4\,H^+$	-21.01 ± 0.02

In acid solutions, where $-4.5 \leq \log h \leq -1.0$, the main species are H_2Asc, $HAsc^-$, and $CdHAsc^+$. In neutral solutions, where $-6.5 \leq \log h \leq -4.5$, the predominating species are $HAsc^-$, $CdHAsc^+$, Cd_2Asc^{2+}, and Cd_4Asc_4. At the lowest values of log h studied, $Cd_5Asc_4OH^+$ seems to be important. Complexes with 3 Cd(II), found in part III,[3] are also present, but in small amounts. In this investigation, where the total concentration of Cd(II) was much higher than in part III,[3] Cd_4Asc_4 predominates over Cd_3Asc_3. Since in this study $B/C \geq 5$, the complexes $Cd_5Asc_6^{2-}$, $Cd_5Asc_6H^-$, or $Cd_3Asc_4H^-$ (*cf.* part III [3])

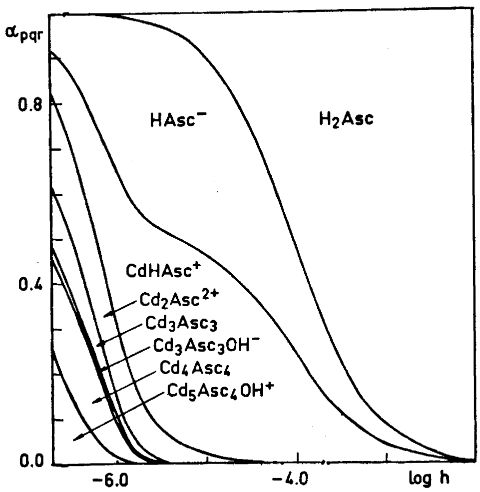

Fig. 7 a. The distribution of ascorbic acid on different species as a function of log h. $B = 0.4$ and $C = 0.02$ M. HALTAFALL [14] was used for the calculations, taking the constants from Table 5. At a given value of log h, the fraction of ascorbic acid present as $H_pB_qC_r$ is presented by the segment of a vertical line falling within the corresponding area.

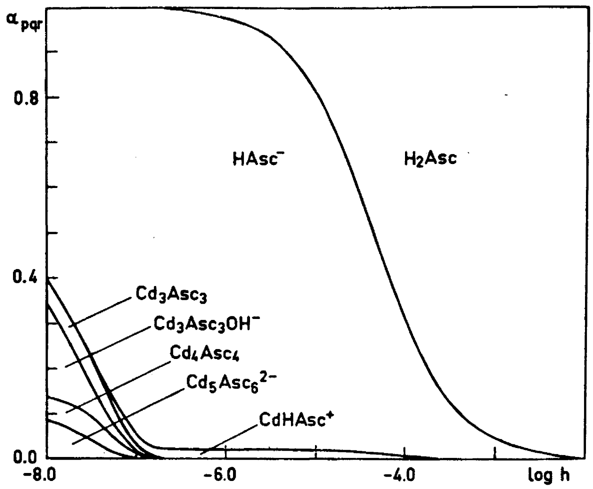

Fig. 7 b. The distribution of ascorbic acid on different species as a function of log *h*. $B = 0.01$ M and $C = 0.02$ M. HALTAFALL [14] was used for the calculation taking the constants from Table 5 and Ref. 3 ($\beta_{\bar{6}56}$).

are certainly not important here. This has been checked by HALTAFALL [14] calculations, using the formation constants determined by us. Distribution diagrams of ascorbic acid on different species is shown in Fig. 7. Veselinović and Sušić [16] have also found that $CdHAsc^+$ predominates in acid solutions ($\log \beta_{011} = 1.3$).

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