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Equilibrium Studies of L-Ascorbate Ions

III. Equilibria between Cadmium(II) Ions, Ascorbate Ions and Protons in 3 M (Na)ClO_4 Medium

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Potentiometric titrations were carried out to give 559 experimental points at 25°C using glass electrodes. The concentration ranges studied are $0.00125 \leq [Cd^{2+}]_{tot} \leq 0.2$ M, $0.005 \leq [H_2Asc]_{tot} \leq 0.2$ M, and $-8.7 \leq \log [H^+] \leq -1.3$, where $H_2Asc \equiv$ ascorbic acid.

In acid solutions, where $-5.0 \leq \log [H^+] \leq -1.3$, the most important species seem to be H_2Asc, $HAsc^-$, and $CdHAsc^+$.

In neutral solutions, where $-8.7 \leq \log [H^+] \leq -5.0$, the data indicate the species $HAsc^-$, $CdHAsc^+$, Cd_3Asc_3, and $Cd_5Asc_6^{2-}$. By reaction with OH^- or H^+ the last two species form $Cd_3Asc_3OH^-$ and $Cd_5Asc_6H^-$.

We also found evidence for $Cd_3Asc_4H^-$ and Cd_4Asc_4.

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.

Our main task is to find the predominating species in the solution. The equilibrium reaction for the formation of a complex $H_pB_qC_r$ can be written:

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

In part I[1] of this series we have studied the equilibria between ascorbic acid and H^+ in 3 M $NaClO_4$. We found $pK_{a_1} = 4.36$ and $pK_{a_2} = 11.34$. At high concentrations of ascorbic acid (≥ 0.25 M) dimers H_4Asc_2 and $H_3Asc_2^-$ must be considered. In part II[2] a literature survey of metal ascorbate complexes and an introduction to the experimental technique and the methods of calculation have been given.

SYMBOLS

For a complete list, see part II.[2] The most common symbols are H, B, C for H^+, Cd^{2+}, and $HAsc^-$ ($\equiv$ the ion of ascorbic acid with the proton dissociated), respectively. H = the excess (analytical) concentration of hydrogen

ions over H_2O, Cd^{2+}, and $HAsc^-$. The total concentrations of B and C we denote B and C. The analytical concentrations in the starting solution S_0 we write H_0, B_0, and C_0, and those in the buret solution T H_T, B_T, and C_T. The concentrations of free H, B, and C we write h, b, and c. Z = the average number of H^+ bound per C. $Z_{H/B}$ = the average number of H^+ bound per B. $Z_{C/B}$ = the average number of C bound per B. $C_{noB} = [H_2Asc] + [HAsc^-]$ and $Z_{noB}C_{noB} = [H_2Asc]$. (V,E) = volume and emf measured.

EXPERIMENTAL

Chemicals and analysis

Most of the chemicals and the solutions were prepared and analysed as described in the previous parts I [1] and II,[2] where also a description of saltbridges, electrodes, potentiometer and thermostat is found.

$Cd(ClO_4)_2$ was mostly prepared according to Biedermann and Ciavatta.[4] $Cd(NO_3)_2(H_2O)_4$ from Baker was recrystallized twice. Cadmium nitrate was gradually heated to 400°C and then ignited at 800°C for 12 h. A stock solution of $Cd(ClO_4)_2$ was prepared by dissolving CdO in $HClO_4$. $NaClO_4$ was then added to 6 M.

Cadmium perchlorate was also prepared by means of a cation exchanger, saturating with cadmium nitrate solution, washing with water, and eluting with a sodium perchlorate solution.

In none of the $Cd(ClO_4)_2$ solutions so prepared could we detect any Cl^-, SO_4^{2-}, NO_3^- or Fe^{3+}. Using different stock solutions, no difference could be seen in the measurements.

The concentration of Cd^{2+} in a stock solution was determined gravimetrically as $CdNH_4PO_4H_2O$.[5] In one case, the stock solution of Cd^{2+} was also analysed by electrolysis in a KCN solution.[5] Different determinations agreed within ±0.1 %. The excess hydrogen ion concentration (H) of the stock solution, ~0.02 M, we determined by titrations, using a standardized sodium hydroxide solution, and methyl red as indicator. The Cd^{2+} ion is a very weak acid [4] and does not influence this determination of H^+. A check of H was later obtained in the Gran extrapolations [6] used in the acid part of each titration of equilibrium mixtures of $H^+ - Cd^{2+} - HAsc^-$.

The concentration of ClO_4^- (~6 M) in a stock solution of $Cd(ClO_4)_2$ was determined by means of a cation exchanger, which was saturated with perchloric acid. After washing with water, a measured quantity of the stock solution was passed through a column, filled with the cation exchanger, followed by water until the eluate was neutral. The collected eluate was titrated with a standard sodium hydroxide solution. Determinations of $[H^+]$ in the same solution agreed within ±0.1 %, and the determination of $[ClO_4^-]$ agreed within ±0.2 %.

Emf measurements and titration procedure

The cell used to measure $[H^+]$ and the procedure of mixing solutions have been described in part II.[2] As reference electrode we used RE = 3 M $NaClO_4$| 2.900 M $NaClO_4$, 0.010 M NaCl, saturated with AgCl|AgCl, Ag (alt. 1 in part II,[2] but here written as − pole).

In our experiments we have used 6 different *glass electrodes*, picked out from 8 Beckman 41260 electrodes.

We could not get a stable potential of a *hydrogen electrode* in equilibrium solutions containing Cd(II) and ascorbic acid. Quinhydrone reacts with ascorbic acid, so neither can the *quinhydrone electrode* be used in our solutions.

The emf of the glass electrode cell mostly reached a constant value within 5 min. At the last points of a forward titration,[2] where pH ≈ 8, however, we often had to wait 30 or 45 min to get a constant emf. We checked the emf every 10 min. If the emf was constant within ±0.1 mV for 10 min, it was accepted. We tested the constancy of a few points after 12 h. The shift was not greater than 0.3 mV. For $-H > B$, a yellow precipitate

sometimes formed within 12 h. In neutral solutions, that is $5 \leq pH \leq 8$, the equilibrium solution was yellow, but in two experiments the colour shifted to orange and a faint opalescence appeared. The titration was then interrupted, and new titration solutions were prepared from new stock solutions. In the next titration, neither orange colour nor opalescence appeared. Presumably the solutions are very sensitive to traces of oxygen. All solutions were prepared using deaerated water and were kept in a nitrogen atmosphere.

In Fig. 1 is seen that the reproducibility was very good. Back titrations show that the equilibria are reversible.

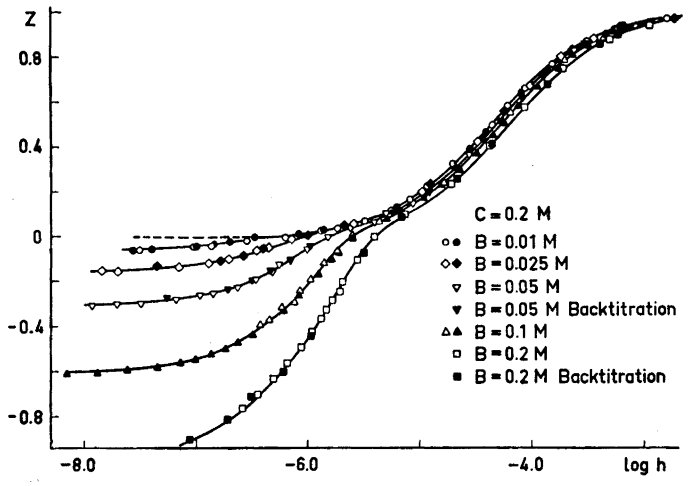

Fig. 1. Z (= the average number of H^+ bound per $HAsc^-$) as a function of $\log h$. The curves have been calculated from the final values of the formation constants using HALTAFALL.[13] The broken line corresponds to the Z-curve for ascorbic acid when Cd(II) is absent.

SURVEY OF EXPERIMENTAL DATA

For each titration, E_0 was calculated and H_0 or H_T were corrected, using a few acid points.

These calculations, described in part II,[2] were performed using the computer program TRAVE.[3] From the primary data $(V,E)_{B,C}$, that is volumes, emf values, and analytical concentrations, we have calculated $(H,h)_{B,C}$ and $Z(\log h)_{B,C}$ from eqns. (2), (3), and (4) (Fig. 1 and Table 1 a). H_{calc} has been obtained from the general eqns. (5 a – c), knowing B, C, h, and eliminating b and c. Z_{calc} can then be calculated from $C\ Z_{calc} = H_{calc} - h + K_w h^{-1}$.

$$E = E_0 + 59.155 \log h + E_j \qquad E_j = -17\ h \tag{2}$$

$$H = (V_0 H_0 + V H_T)/(V + V_0) \tag{3}$$

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

$$H = h + \sum p\beta_{pqr} h^p b^q c^r \tag{5 a}$$

$$B = b + \sum q\beta_{pqr} h^p b^q c^r \tag{5 b}$$

$$C = c + \sum r\beta_{pqr} h^p b^q c^r \tag{5 c}$$

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 30.03 ml of a solution with total concentrations H_0, B_0, and C_0; E, log [H$^+$] (≡"LOG A"); H (≡"ATOT") and $(H_{calc} - H)10^3$ (≡"DATOT"). H_{calc} was calculated using the equilibrium constants in Table 5, and the systematic errrors δH and the final values of E_0 in Table 1 b.

SATS 1

V	E(MV)	LOGA	ATOT(MM	DATOT
0,00	242,60	-1,533	34,24	0,06
10,12	230,50	-1,741	23,25	-0,10
20,07	219,60	-1,927	16,77	0,04
30,17	207,60	-2,131	12,39	-0,02
40,02	194,20	-2,358	9,33	0,00
50,04	175,10	-2,682	6,99	-0,01
60,14	141,20	-3,255	5,16	0,04
70,02	108,00	-3,952	3,72	0,01
80,10	70,20	-4,388	2,53	-0,04
90,22	51,70	-4,768	1,52	-0,08
100,24	21,80	-5,274	0,69	-0,13
110,25	-159,30	-8,335	-0,41	-0,07
110,20	-162,40	-8,388	-0,53	-0,04
120,16	-165,40	-8,439	-0,65	-0,02
122,36	-167,90	-8,481	-0,77	0,03
124,16	-170,50	-8,525	-0,87	0,06
126,20	-172,10	-8,552	-0,98	0,13
128,20	-175,30	-8,606	-1,09	0,14

SATS 2

V	E(MV)	LOGA	ATOT(MM	DATOT
0,30	243,28	-1,533	34,42	-0,10
10,02	231,70	-1,738	23,52	0,08
20,07	220,70	-1,918	16,97	0,09
30,10	209,20	-2,114	12,61	0,06
40,12	196,00	-2,338	9,50	0,04
50,14	178,30	-2,638	7,17	0,04
60,18	148,20	-3,147	5,36	0,07
70,20	116,70	-3,849	3,91	0,08
80,22	79,80	-4,303	2,72	0,02
90,24	58,00	-4,672	1,73	-0,05
100,34	32,40	-5,105	0,89	-0,11
106,28	5,00	-5,568	0,45	-0,15
122,36	-145,80	-8,104	-0,56	-0,09
124,36	-147,20	-8,141	-0,67	-0,08
126,46	-149,20	-8,175	-0,78	-0,07
128,36	-150,00	-8,188	-0,88	-0,01
130,56	-152,50	-8,230	-1,00	-0,03
132,48	-153,80	-8,252	-1,09	-0,00
134,58	-155,10	-8,274	-1,20	0,03
136,50	-156,60	-8,300	-1,29	0,05
138,60	-158,30	-8,328	-1,39	0,05
140,50	-160,00	-8,357	-1,47	0,05
142,42	-161,60	-8,384	-1,56	0,05
146,46	-166,00	-8,459	-1,73	0,00

SATS 3

V	E(MV)	LOGA	ATOT(MM	DATOT
0,30	250,30	-1,530	34,57	-0,09
9,84	239,80	-1,724	23,75	0,18
20,06	227,70	-1,917	17,01	0,06
30,12	216,10	-2,115	12,62	0,03
40,10	202,90	-2,339	9,50	0,03
50,22	184,30	-2,654	7,14	-0,01
58,22	160,40	-3,058	5,65	-0,01
64,16	134,00	-3,505	4,71	-0,00
70,18	111,10	-3,892	3,97	0,00
76,16	94,70	-4,169	3,13	-0,05
80,18	85,40	-4,326	2,68	-0,02
88,18	66,30	-4,616	1,97	-0,04
96,32	49,10	-4,940	1,15	-0,09
104,24	21,00	-5,415	0,54	-0,12
116,28	-109,00	-7,613	-0,27	0,10
118,32	-114,20	-7,701	-0,39	0,08
120,22	-116,10	-7,767	-0,51	0,04
122,30	-122,00	-7,832	-0,63	-0,04
124,22	-124,10	-7,868	-0,73	-0,06
128,22	-127,70	-7,929	-0,95	-0,08
132,34	-129,80	-7,964	-1,16	-0,02
136,22	-131,40	-7,991	-1,35	0,04
140,22	-133,10	-8,020	-1,54	0,10

SATS 4

V	E(MV)	LOGA	ATOT(MM	DATOT
0,00	263,90	-1,257	75,03	0,38
0,70	262,30	-1,285	72,27	-0,48
2,00	260,10	-1,323	67,47	0,01
4,30	255,70	-1,400	59,86	-0,07
9,12	246,00	-1,568	46,82	0,22
12,04	239,00	-1,688	40,37	0,11
15,03	230,50	-1,833	34,63	-0,01
18,14	219,20	-2,026	29,42	-0,09
24,08	173,70	-2,797	21,13	-0,07
28,08	120,30	-3,730	16,51	0,11
32,05	94,80	-4,131	12,50	0,19
36,45	74,60	-4,473	8,62	0,13
39,78	59,20	-4,733	6,82	-0,04
43,78	37,40	-5,102	3,19	-0,11
46,79	7,80	-5,602	1,26	-0,17
49,80	-74,30	-6,990	-0,52	0,05
50,80	-81,40	-7,110	-1,09	0,04
50,80	-81,50	-7,112	-1,09	0,03
51,69	-86,30	-7,193	-1,69	0,03
53,81	-93,30	-7,311	-2,70	-0,06
55,85	-99,30	-7,413	-3,73	-0,11
58,52	-106,40	-7,533	-5,01	-0,16
61,02	-112,20	-7,631	-6,14	-0,09
63,30	-117,10	-7,713	-7,11	0,04
64,83	-120,90	-7,778	-7,74	0,06
66,39	-124,50	-7,839	-8,36	0,13
67,83	-129,50	-7,923	-8,92	-0,02
69,94	-135,50	-8,025	-9,70	0,01

SATS 5

V	E(MV)	LOGA	ATOT(MM	DATOT
0,00	254,20	-1,402	89,74	-0,21
1,00	251,30	-1,454	85,24	-0,18
2,18	247,70	-1,517	80,29	0,08
3,60	242,60	-1,604	74,79	-0,01
6,20	231,40	-1,796	65,84	0,01
8,10	220,00	-1,991	60,07	-0,06
10,32	198,00	-2,351	54,91	-0,04
12,12	167,00	-2,889	49,57	0,08
13,04	149,70	-3,182	47,45	0,18
14,64	130,20	-3,512	43,96	0,15
16,82	114,60	-3,775	39,49	0,27
19,24	102,70	-3,977	35,19	0,31
22,76	90,00	-4,191	29,51	0,38
26,08	80,00	-4,360	24,91	0,26
30,08	69,70	-4,534	19,44	0,28
34,22	59,30	-4,710	15,34	0,15
36,12	54,40	-4,793	13,46	0,06
38,22	49,00	-4,884	11,51	0,04
40,10	43,80	-4,972	9,86	-0,01
42,10	37,80	-5,074	8,21	-0,07
44,50	29,70	-5,211	6,33	-0,12
47,10	18,90	-5,393	4,44	-0,18
49,50	5,30	-5,623	2,79	-0,20
51,32	-10,40	-5,888	1,61	-0,17
52,32	-23,80	-6,115	0,99	-0,13
53,42	-41,80	-6,419	0,32	0,01
54,82	-58,90	-6,708	-0,51	-0,10
55,92	-62,60	-6,771	-0,97	-0,06
57,02	-69,20	-6,882	-1,93	-0,14
58,74	-72,70	-6,942	-2,70	-0,04
59,74	-75,20	-6,984	-3,22	-0,02
61,14	-78,50	-7,040	-3,94	0,00
63,16	-83,20	-7,119	-4,94	0,00
67,18	-92,80	-7,281	-6,80	-0,03
68,70	-96,50	-7,344	-7,46	-0,02
70,18	-100,50	-7,412	-8,09	-0,03
72,40	-107,20	-7,525	-9,00	-0,06
75,22	-118,20	-7,711	-10,10	-0,14
80,20	-148,50	-8,223	-11,90	-0,04

SATS 6

V	E(MV)	LOGA	ATOT(MM	DATOT
0,00	262,10	-1,311	99,11	-0,29
2,14	257,30	-1,395	90,24	0,02
6,08	247,20	-1,569	76,46	0,22
10,10	234,00	-1,795	65,56	0,32
14,10	213,70	-2,141	56,52	0,48
18,22	166,31	-2,944	48,77	0,45
NEW BURET				
1,09	140,90	-3,374	45,94	0,55
2,18	125,62	-3,632	41,47	0,64
5,10	100,80	-4,052	32,42	0,61
8,08	83,20	-4,349	24,53	0,41
15,20	42,63	-5,036	8,49	-0,19
17,08	22,32	-5,379	4,59	-0,31
18,10	5,40	-5,658	2,67	-0,34
19,30	+28,00	-6,229	0,48	-0,24
20,36	+42,30	-6,471	-1,38	-0,33
22,06	+51,40	-6,625	-4,26	-0,28
24,38	+59,20	-6,756	-7,50	-0,13
26,18	+66,10	-6,873	-10,68	0,01
28,50	+73,30	-6,995	-13,71	-0,06
30,14	+79,60	-7,101	-16,21	-0,11
32,20	+87,15	-7,229	-19,68	-0,21
34,22	+95,30	-7,367	-21,36	-0,31
37,14	-108,70	-7,593	-24,74	-0,29
40,12	-129,70	-7,948	-27,96	-0,47

SATS 7

V	E(MV)	LOGA	ATOT(MM	DATOT
0,00	261,70	-1,396	99,62	-0,26
2,10	257,70	-1,476	91,99	0,04
6,18	249,10	-1,525	79,69	0,15
10,12	239,50	-1,690	70,18	0,12
14,22	227,00	-1,903	62,09	0,19
18,34	208,60	-2,216	55,34	0,30
22,05	179,10	-2,716	50,17	0,39
NEW BURET				
1,06	155,70	-3,112	47,12	0,41
2,02	140,30	-3,372	44,47	0,36
4,70	120,40	-3,709	39,27	0,26
8,16	95,50	-4,130	29,47	-0,28
12,08	78,10	-4,424	21,39	-0,58
16,14	60,50	-4,721	14,01	-0,78
20,14	38,90	-5,088	7,55	-0,84
24,16	4,30	-5,672	1,74	-0,12
26,68	+14,10	-5,983	-1,60	-0,22
30,16	+23,70	-6,145	-5,88	-0,42
34,22	+29,70	-6,246	-10,44	0,16
38,22	+34,90	-6,334	-14,52	0,38
43,56	+40,90	-6,436	-19,27	0,50
49,34	+47,80	-6,552	-24,19	0,22
53,32	+52,10	-6,625	-27,15	0,12

SATS 8

V	E(MV)	LOGA	ATOT(MM	DATOT
0,00	256,10	-1,410	139,05	-0,29
0,80	252,10	-1,480	133,54	-0,53
1,72	247,20	-1,564	127,54	-0,42

Table 1 a. Continued.

2,58	241,90	+1,655	122,24	+0,32
4,02	230,70	+1,847	113,96	+0,04
5,62	210,70	+2,187	105,55	0,28
7,50	163,60	+2,985	96,59	0,41
9,30	136,10	+3,450	88,80	0,61
11,14	121,30	+3,700	81,55	0,72
14,14	106,10	+3,957	71,03	0,80
18,14	92,10	+4,194	59,03	0,57
22,18	81,20	+4,378	48,78	0,32
26,18	72,90	+4,534	40,08	0,19
32,18	59,20	+4,750	29,13	+0,06
40,12	41,90	+5,043	17,52	+0,23
44,24	31,20	+5,223	12,47	+0,36
48,12	19,10	+5,428	8,21	+0,28
52,24	+0,20	+5,754	4,12	+0,22
54,34	+16,40	+6,028	2,19	+0,11
55,78	+31,80	+6,288	0,92	+0,01
57,26	+44,10	+6,496	+0,34	+0,04
58,20	+49,00	+6,579	+1,12	+0,07
59,50	+54,10	+6,665	+2,17	+0,06
60,68	+58,30	+6,736	+3,10	+0,08
61,80	+61,90	+6,797	+3,96	+0,05
62,98	+65,80	+6,863	+4,84	+0,05
64,32	+70,30	+6,939	+5,81	+0,05
66,00	+76,70	+7,047	+7,00	+0,10
67,70	+83,70	+7,166	+8,15	+0,09
68,92	+89,70	+7,267	+8,96	+0,09
70,12	+97,30	+7,396	+9,73	+0,14
71,42	+108,10	+7,578	+10,55	+0,16
72,72	+124,60	+7,857	+11,34	+0,17
74,24	+152,80	+8,334	+12,25	0,07

SATS 9

V	E(MV)	LOGA	ATOT(MM)	DATOT
0,00	259,10	+1,509	146,58	0,37
1,30	256,20	+1,560	143,68	+0,05
2,30	254,10	+1,596	140,04	+0,02
5,10	247,90	+1,704	131,16	0,04
9,02	238,00	+1,874	120,86	0,10
14,02	221,20	+1,961	110,39	0,14
21,36	173,40	+2,772	98,70	0,38

New Buret

2,20	137,50	+3,379	98,18	0,48
2,60	133,30	+3,450	88,79	0,36
6,02	111,10	+3,825	76,92	0,04
10,02	95,70	+4,086	64,81	+0,16
20,04	69,90	+4,522	40,43	+0,29
30,06	46,70	+4,914	22,04	0,69
40,00	15,99	+5,435	7,79	+0,20
43,90	-7,60	+5,632	3,01	0,04
47,92	+32,60	+6,755	+1,53	+0,16
52,10	+42,70	+6,425	+5,87	+0,15
54,02	+46,40	+6,488	+7,75	+0,15
55,92	+49,80	+6,545	+9,54	+0,12
58,02	+53,10	+6,601	+11,45	0,09
59,94	+56,50	+6,659	+13,13	0,06
61,94	+59,90	+6,716	+14,83	0,12

New Buret

0,60	+65,00	+6,802	+16,99	+0,00
1,00	+66,30	+6,858	+18,42	0,07
2,10	+79,80	+7,052	+22,29	0,01
3,02	+92,90	+7,274	+25,48	0,07
3,52	+105,60	+7,489	+27,19	+0,20
4,02	+121,90	+7,764	+28,89	+0,06
4,32	+138,00	+8,036	+29,90	0,06

SATS10

V	E(MV)	LOGA	ATOT(MM)	DATOT
0,00	268,30	+1,311	148,52	0,20
2,28	262,80	+1,407	139,16	+0,12
6,00	253,20	+1,573	126,42	0,13
10,04	240,00	+1,799	115,27	0,32
14,18	220,30	+2,135	105,96	0,76
18,04	183,20	+2,764	98,72	0,44

New Buret

2,00	145,50	+3,401	89,51	0,66
4,00	127,40	+3,707	81,02	0,47
6,02	115,70	+3,905	73,07	0,45
10,04	99,00	+4,187	58,90	0,23
15,10	82,70	+4,463	43,62	+0,20
20,08	68,20	+4,708	30,81	+0,40
24,12	55,30	+4,918	21,71	+0,46
28,10	41,00	+5,168	13,69	+0,51
32,06	20,00	+5,523	6,50	+0,23
34,16	1,19	+5,842	2,97	+0,01
35,10	+9,70	+6,025	1,44	0,02
37,18	+24,50	+6,275	+1,81	+0,32
40,14	+34,10	+6,437	+6,17	+0,22
42,64	+40,70	+6,549	+9,63	+0,15
45,28	+47,70	+6,667	+13,08	+0,25
45,68	+48,80	+6,686	+13,59	+0,27
48,28	+55,70	+6,803	+16,78	+0,22
52,20	+67,60	+7,004	+21,27	+0,13
56,30	+85,50	+7,306	+25,62	+0,15
60,30	+122,30	+7,928	+29,53	+0,00

SATS11

V	E(MV)	LOGA	ATOT(MM)	DATOT
0,00	265,00	+1,308	149,04	0,02
2,06	260,90	+1,380	141,63	+0,06
5,00	254,90	+1,484	132,58	0,09
10,04	242,80	+1,692	120,15	+0,08
15,02	227,20	+1,958	110,59	+0,07
18,06	213,60	+2,190	105,74	+0,09
22,14	187,30	+2,635	100,10	+0,05

New Buret

1,30	161,10	+3,079	94,90	+0,09
2,00	152,60	+3,222	92,20	0,21
4,00	134,60	+3,527	84,86	0,23
8,02	113,90	+3,877	71,58	0,02
14,04	95,10	+4,195	54,71	0,16
20,10	80,10	+4,448	40,57	+0,05
25,06	68,80	+4,639	30,64	+0,08
32,00	51,70	+4,928	18,72	+0,22
40,04	24,80	+5,383	7,15	+0,02
43,34	11,30	+5,611	2,97	0,07
45,34	5,60	+5,708	0,57	0,09
47,44	1,30	+5,780	+1,85	0,02
51,30	+4,20	+5,873	+6,03	+0,18

SATS12

V	E(MV)	LOGA	ATOT(MM)	DATOT
0.000	265,10	+1,263	255,18	+0,77
0.080	264,30	+1,277	253,14	+0,46
0.200	263,00	+1,300	250,10	+0,13
0.402	260,10	+1,350	245,03	+0,68
0.728	255,10	+1,437	236,99	+0,69
1.000	250,30	+1,520	230,42	+0,52
1.296	244,00	+1,629	223,39	+0,24
1.680	233,50	+1,858	214,47	0,52
1.996	217,40	+2,083	207,29	+0,07
2.416	183,10	+2,664	197,96	0,26
2.618	157,00	+3,106	189,26	0,99
3.196	142,60	+3,349	181,77	1,44
3.598	132,00	+3,529	172,97	1,69
4.218	120,30	+3,726	160,54	2,02
4.996	109,00	+3,917	145,58	1,66
5.976	98,10	+4,102	127,65	1,55
6.974	88,50	+4,264	110,36	0,99
7.974	79,50	+4,416	93,95	+0,04
8.976	71,10	+4,558	78,36	+0,41
9.976	62,20	+4,719	63,97	+1,32
11.436	48,40	+4,942	43,26	+1,46
12.816	31,70	+5,224	25,34	+1,00
13.976	7,60	+5,632	11,14	+0,90
14.378	-6,70	+5,873	6,40	+0,45
14.616	+19,20	+6,085	3,63	+0,20
14.876	+34,60	+6,345	0,63	+0,36
15.056	+43,30	+6,487	+1,42	+0,53
15.296	+53,00	+6,656	+4,13	+0,45
15.516	+64,20	+6,845	+6,61	+0,39
15.684	+74,80	+7,025	+8,45	+0,22
15.878	+97,40	+7,407	-10,58	+0,14
15.974	+107,20	+7,572	-11,63	0,43

SATS13

V	E(MV)	LOGA	ATOT(MM)	DATOT
0,00	262,70	+1,338	244,29	1,44
1,04	257,80	+1,423	237,03	0,48
1,98	253,30	+1,501	230,86	0,41
4,04	240,60	+1,719	218,55	0,08
6,06	220,80	+2,057	207,84	+0,06
7,22	201,90	+2,378	202,71	+0,08
8,58	176,70	+2,805	196,05	0,11
11,18	149,80	+3,260	185,40	0,48
14,09	135,10	+3,508	174,96	0,75

New Buret

2,00	116,50	+3,023	154,00	1,30
4,20	102,40	+4,061	132,96	0,48
6,00	93,50	+4,211	117,11	0,17
7,94	85,00	+4,355	101,26	+0,33
10,10	76,20	+4,504	84,94	+0,98
13,06	64,50	+4,702	64,58	+1,65
16,12	51,70	+4,918	45,64	+2,00
18,24	41,70	+5,087	33,61	+1,79
19,96	32,00	+5,251	24,43	+1,46
21,86	18,50	+5,479	14,85	+0,60
23,16	3,00	+5,741	8,60	+0,57
23,68	-4,80	+5,873	6,17	+0,23
24,58	+24,20	+6,201	2,05	0,10
25,16	+35,10	+6,385	+0,54	0,21
25,78	+44,70	+6,548	+3,27	0,35
26,48	+58,30	+6,770	+6,30	0,08
27,12	+72,50	+7,018	+9,01	0,39
27,68	+101,80	+7,513	+11,35	0,38

SATS14

V	E(MV)	LOGA	ATOT(MM)	DATOT
0,00	262,20	+1,300	248,92	1,00
2,08	257,40	+1,384	240,37	0,73
5,02	250,00	+1,512	230,02	0,45
8,14	240,90	+1,668	220,77	0,26
11,04	230,30	+1,850	213,44	0,05
14,02	215,90	+2,095	206,91	0,01
18,10	187,80	+2,571	199,28	0,08

New Buret

2,30	135,70	+3,453	176,30	1,36
4,12	119,00	+3,735	159,55	1,32
7,00	102,30	+4,018	135,29	1,09
10,01	74,80	+4,482	85,66	+0,74
17,64	62,00	+4,699	64,12	+2,12
22,08	46,10	+4,968	40,80	+1,78
26,08	27,70	+5,279	22,17	+0,99
28,60	9,70	+5,583	11,44	+0,44
30,14	+6,80	+5,862	5,22	+0,23
32,12	+23,30	+6,141	+2,43	+0,35
34,14	+35,60	+6,349	+9,85	+0,38
35,14	+41,80	+6,454	+13,39	+0,30
36,14	+48,20	+6,562	+16,84	0,02
37,14	+56,50	+6,702	+20,22	0,04
38,13	+66,70	+6,874	+23,48	0,18
39,14	+82,90	+7,148	+26,74	0,24
40,12	+115,20	+7,694	+29,83	0,56

SATS15

V	E(MV)	LOGA	ATOT(MM)	DATOT
0,00	258,00	+1,293	250,36	0,40
2,30	253,00	+1,380	241,20	0,26
5,08	246,70	+1,489	231,73	0,41

Table 1 a. Continued.

9,20	235,30	+1,685	220,16	0,84
14,02	217,70	+1,986	209,37	0,89
18,34	192,70	+2,410	201,53	0,86
21,36	173,10	+2,742	196,83	0,11
24,06	160,60	+2,954	193,07	0,23
30,14	144,10	+3,233	185,84	0,40
NEW BUREET				
1,98	119,80	+3,644	166,10	1,02
4,10	104,50	+3,902	146,31	0,98
8,10	84,30	+4,244	112,31	+0,21
13,00	64,40	+4,580	75,73	+1,55
17,74	45,30	+4,903	44,72	+0,85
22,06	21,00	+5,314	19,57	0,12
24,10	1,20	+5,649	8,59	0,84
25,60	+20,20	+6,010	8,86	0,53
26,96	+30,20	+6,180	+3,96	+0,19
28,06	+43,20	+6,399	+11,27	+0,68
29,16	+53,10	+6,567	+16,47	+0,48
30,16	+65,40	+6,775	+21,09	+0,53
31,16	+84,70	+7,191	+25,61	+0,45
31,96	+99,30	+7,348	+27,39	+0,58
32,87	-128,40	+7,840	+29,64	0,04

SATS16

V	E(HV)	LOGA	ATOT(MM)	DATOT
0,00	264,40	+1,284	251,11	0,72
1,00	262,60	+1,315	247,18	1,00
2,00	260,60	+1,350	243,40	0,94
5,10	253,90	+1,466	233,39	0,49
9,12	243,90	+1,639	222,67	+0,11
14,04	228,30	+1,906	212,22	+0,55
NEW BUREET				
4,08	127,20	+3,618	166,76	0,45
10,08	91,30	+4,225	112,36	+0,62
19,98	51,70	+4,894	44,89	+1,87
24,14	28,90	+5,280	22,18	+1,94
30,94	+13,20	+5,992	+9,21	+0,56
34,36	+25,20	+6,194	+22,78	+0,10
36,16	+32,10	+6,311	+29,62	+0,05
38,20	+40,80	+6,458	+36,85	+0,13
40,00	+50,00	+6,614	+43,00	+0,16
41,98	+63,30	+6,838	+49,47	+0,15
42,79	+70,30	+6,957	+52,00	+0,05
43,75	+81,20	+7,141	+55,10	0,24
44,93	+101,40	+7,483	+58,49	0,58
45,34	+113,90	+7,694	+59,79	0,83
45,68	+126,90	+7,914	+60,80	1,10

SATS17

V	E(HV)	LOGA	ATOT(MM)	DATOT
0,00	+97,90	+7,282	+55,02	+1,35
0,55	+65,80	+6,739	+46,16	+0,93
1,02	+52,80	+6,519	+38,83	+0,76
1,53	+43,00	+6,353	+31,12	+0,80
2,23	+32,50	+6,176	+20,95	+0,79
3,05	+22,10	+6,000	+9,57	+0,76
3,75	+11,90	+5,828	-0,30	0,31
4,30	0,00	+5,627	6,73	1,51
4,85	12,20	+5,420	13,53	1,34
5,50	23,00	+5,238	21,29	0,81
6,25	32,30	+5,081	29,91	0,42
7,17	41,00	+4,933	40,00	0,08
8,27	49,30	+4,793	51,43	+0,06
9,28	55,70	+4,685	61,36	0,01
10,53	62,40	+4,572	72,97	+0,06
12,07	69,50	+4,452	86,32	+0,31
14,14	78,30	+4,313	102,80	0,11
17,06	89,70	+4,110	123,58	0,83
20,05	101,00	+3,919	142,35	1,28
25,05	122,00	+3,564	169,19	1,32
30,12	157,30	+2,967	191,84	0,72
35,07	218,00	+1,938	210,56	0,14
37,19	229,00	+1,750	217,44	+0,20
39,15	236,60	+1,620	223,97	+0,38
41,15	242,00	+1,527	229,98	+0,60
43,15	246,20	+1,455	235,67	+0,83
45,15	249,60	+1,396	241,05	+1,07

SATS18

V	E(HV)	LOGA	ATOT(MM)	DATOT
0,00	263,00	-1,292	250,49	0,30
2,06	258,90	-1,364	242,97	0,04
5,00	253,80	-1,466	233,77	0,09
10,02	241,70	+1,661	221,19	0,15
14,02	230,10	-1,859	213,22	+0,16
18,10	214,20	-2,130	206,45	+0,47
22,14	194,60	-2,462	200,79	+0,40
NEW BUREET				
1,42	157,90	-3,084	187,83	0,84
2,66	141,20	-3,366	177,06	1,39
4,98	120,40	+3,718	158,17	+1,14
8,24	106,20	+3,958	134,08	1,67
12,02	92,20	+4,194	109,20	1,29
18,28	73,10	+4,517	73,88	0,59
23,64	56,90	+4,791	48,27	+0,01
28,38	39,90	+5,079	28,47	+0,29
32,20	23,20	+5,361	14,12	0,32
36,22	8,80	+5,694	0,37	+0,23
40,08	1,00	+5,736	+11,71	+0,52
44,18	+5,40	+5,844	+23,48	+0,57
49,70	+12,90	+5,971	+37,83	+0,33
53,78	+18,30	+6,062	+47,48	+0,39
56,22	+21,60	+6,118	+52,90	+0,59
58,90	+25,00	+6,176	+58,58	+0,43
60,76	+27,20	+6,213	+62,36	+0,06
63,66	+31,10	+6,279	+68,02	+0,14
66,66	+35,20	+6,348	+73,58	+0,18
69,66	+39,60	+6,422	+78,87	+0,41

SATS19

V	E(HV)	LOGA	ATOT(MM)	DATOT
0,000	264,40	+1,318	251,99	+4,10
0,446	259,10	+1,410	240,80	+2,17
0,600	257,00	+1,446	237,02	+1,54
0,814	252,90	+1,517	231,82	+1,78
1,116	246,30	+1,631	224,60	+1,66
1,500	234,20	+1,838	215,63	+1,84
1,994	205,40	+2,328	204,40	+1,95
2,992	148,20	+3,296	182,74	+1,26
3,496	135,80	+3,505	172,29	+1,00
3,996	127,00	+3,654	162,23	+0,48
4,520	119,70	+3,778	152,00	0,22
5,400	109,00	+3,959	135,50	0,17
6,436	98,70	+4,133	117,09	0,26
7,220	91,40	+4,256	103,85	+0,32
7,950	85,10	+4,363	92,00	+0,53
9,014	76,20	+4,513	75,53	+0,61
9,988	67,90	+4,653	61,23	+0,56
11,000	58,30	+4,816	47,08	+0,84
11,906	48,80	+4,976	35,00	+0,55
12,436	42,20	+5,088	28,16	+0,51
13,312	29,70	+5,299	17,24	+0,02
14,806	11,30	+5,610	+0,40	0,07
15,876	3,90	+5,735	+12,34	0,19
16,452	0,50	+5,793	+18,53	0,21
17,122	+2,90	+5,850	+25,55	0,83
17,894	+6,70	+5,914	+33,39	1,48
18,668	+10,80	+5,984	+40,92	1,38
19,262	+13,80	+6,034	+46,48	1,72
19,802	+16,80	+6,085	+51,73	1,53
20,290	+19,30	+6,127	+56,19	1,79
21,336	+25,20	+6,227	+65,50	1,79
22,356	+31,50	+6,334	+74,18	1,54
22,972	+36,70	+6,422	+79,27	0,05
23,756	+41,20	+6,498	+85,60	1,24
24,260	+45,10	+6,564	+89,95	1,14
24,784	+49,40	+6,636	+93,59	1,14
25,500	+56,50	+6,756	+98,99	0,76
26,448	+64,05	+6,883	+103,76	0,52
26,798	+72,50	+7,027	+108,43	0,69
27,240	+80,20	+7,157	+111,55	0,64
27,696	+92,00	+7,356	+114,71	0,25
28,176	+108,40	+7,634	+117,99	0,39
28,496	+123,80	+7,894	+120,15	0,75
28,682	+135,10	+8,085	+121,39	1,07

SATS20

V	E(HV)	LOGA	ATOT(MM)	DATOT
0,00	262,00	+1,231	250,81	1,26
2,08	258,00	+1,361	243,05	1,20
5,00	251,80	+1,459	233,71	0,69
9,16	241,60	+1,631	222,40	0,02
14,10	227,10	+1,883	212,53	+0,41
18,12	211,60	+2,146	205,72	+0,38
21,14	196,00	+2,411	201,31	+0,71
NEW BUREET				
0,88	154,30	+2,948	190,81	+0,49
2,00	143,10	+3,306	177,96	+0,39
4,54	118,80	+3,717	150,71	0,02
7,98	99,10	+4,050	117,55	0,51
12,12	80,30	+4,368	82,41	0,26
16,52	60,90	+4,696	49,78	0,48
21,02	36,70	+5,105	20,52	1,63
24,54	19,90	+5,389	+0,05	1,19
28,16	10,80	+5,543	+19,09	+0,25
32,18	3,50	+5,666	+38,41	+0,76
34,08	0,20	+5,722	+46,90	+1,44
36,06	-2,30	+5,764	+55,36	0,14
38,04	-5,40	+5,817	+63,45	+0,15
40,10	-8,40	+5,867	+71,49	0,01
43,20	+13,30	+5,945	+82,92	+0,13
47,20	+18,70	+6,042	+96,61	0,16
52,12	+26,00	+6,165	+112,00	+0,06
57,14	+33,60	+6,293	+126,25	+0,25
62,16	+41,30	+6,427	+139,25	+0,47
67,06	+50,00	+6,571	+150,87	+1,18

SATS21

V	E(HV)	LOGA	ATOT(MM)	DATOT
0,00	+81,40	+7,074	+181,71	+1,58
0,75	+61,00	+6,730	+162,36	+1,32
1,54	+45,30	+6,464	+142,97	+0,11
2,50	+32,00	+6,239	+120,68	0,04
4,03	+16,30	+5,974	+87,75	0,59
8,02	11,20	+5,509	+14,33	0,05
10,05	31,40	+5,168	17,41	1,10
12,53	60,50	+4,676	52,08	+0,86
15,94	78,80	+4,366	83,28	+0,43
17,96	94,00	+4,139	111,30	0,25
20,06	108,10	+3,871	136,31	0,37
22,08	120,30	+3,665	154,76	0,26
24,07	135,10	+3,414	171,68	0,37
25,07	144,90	+3,249	179,60	0,57
30,09	231,90	+1,773	215,74	0,35
34,09	254,20	+1,390	240,48	+0,01
36,11	260,30	+1,283	251,84	0,01
38,12	264,90	+1,202	262,47	0,08
40,08	268,30	+1,142	272,26	+0,39

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 1st buret	2nd buret	3rd buret	E_0 (from acid points)	$E_0 \pm 3\sigma$ refined	10^3 ($\delta H \pm 3\sigma$)
1	0.00125	0.005	0.03425	−0.00936			333.8	333.8 ± 0.2	−0.01 ± 0.07
2	0.0025	0.005	0.03446	−0.00910			334.4	334.4 ± 0.2	−0.05 ± 0.06
3	0.005	0.005	0.03456	−0.00928			341.5	341.3 ± 0.2	0.02 ± 0.05
4	0.01	0.02	0.07502	−0.04610			339.2	339.2 ± 0.2	0.02 ± 0.10
5	0.01	0.05	0.0899	−0.04980			337.7	337.9 ± 0.2	−0.2 ± 0.1
6	0.025	0.05	0.0997	−0.03360	0.1197		340.1	340.5 ± 0.5	−0.6 ± 0.3
7	0.1	0.05	0.1000	−0.01680	−0.1023		339.6	339.8 ± 0.6	−0.4 ± 0.5
8	0.01	0.1	0.1391	−0.0734			339.9	340.2 ± 0.6	−0.1 ± 0.3
9	0.025	0.1	0.1487	0.02870	−0.1089	−0.4251	337.2	337.4 ± 0.3	−0.2 ± 0.3
10	0.025	0.1	0.1492	0.01650	−0.1311		346.4	346.7 ± 0.5	−0.7 ± 0.4
11	0.1	0.1	0.1490	0.03370	−0.1140		343.4	343.2 ± 0.2	0.1 ± 0.2
12	0.01	0.2	0.2549	−0.5135			340.6	340.7 ± 0.7	0.3 ± 0.8
13	0.01	0.2	0.2441	−0.0270	−0.3085		343.1	342.6 ± 0.8	0.2 ± 0.9
14	0.025	0.2	0.2486	0.1166	−0.4050		340.6	340.0 ± 1.0	0.4 ± 1.0
15	0.025	0.2	0.2503	0.1215	−0.4340		335.6	335.4 ± 0.6	0.1 ± 0.6
16	0.05	0.2	0.2502	0.1281	−0.3251		342.2	341.2 ± 0.9	1.0 ± 1.0
17	0.05	0.2	−0.0545	0.4385			331.9	332.8 ± 1.0	−0.6 ± 1.2
18	0.1	0.2	0.2503	0.1332	−0.2885		340.5	340.3 ± 0.8	−0.2 ± 1.1
19	0.1	0.2	0.2510	−0.5133			342.6	343.2 ± 1.2	1.0 ± 1.6
20	0.2	0.2	0.2498	0.1300	−0.4206		339.9	338.7 ± 0.6	1.0 ± 1.1
21	0.2	0.2	−0.1811	0.6130			336.8	337.1 ± 0.7	−0.7 ± 1.2

In our solutions, $[OH^-] = K_w h^{-1} \approx 0$. Using Biedermann and Ciavatta's [4] constants, we found that $[Cd_q(OH)_n] \approx 0$.

We have chosen $B_0 = B_T = B$ and $C_0 = C_T = C$. Thus we keep B and C constant in a titration, while H is varied and can be calculated from eqn. 3.

TREATMENT OF DATA

We have, in the graphical treatment, neglected the species H_pB_q ($p < 0$). In the LETAGROP [9–12] calculations, Biedermann and Ciavatta's constants for cadmium hydrolysis [4] were introduced but not varied.

It was practical first to treat the data from acid solutions and neutral solutions separately, and then to refine the final model using all data.

The Z-curves for log $h > -5$ are approximately parallel, and for various B-values they lie close together (Fig. 1). In this region we may, hence, as a first approximation, assume weak complexes B_qC_r ($p = 0$) to exist.

For log $h < -5$, Z becomes negative and the Z-curves for different B are widely spread, indicating stronger complexes with $p < 0$.

In the graphical treatment we may introduce some approximations, when transforming $(V,E)_{B,C}$ to various functions. In the LETAGROP calculations, however, we always treat the primary data $(V,E)_{B,C}$ directly. From eqns. (2) – (5), the least squares sums $\sum(H_{calc} - H)^2$ or $\sum(Z_{calc} - Z)^2$ were calculated by the special parts of LETAGROP, called PUTS and UBBE.[11,12]

The range $-5.0 \leq \log h \leq -1.3$

If we assume that the predominant metal complexes can be written B_qC_r ($p = 0$), we can calculate $c = [HAsc^-]$, and the average number of C bound per $B = Z_{C/B}$. Since $p = 0$, the average number of H^+ per C in complexes with B ($= Z'_{H/C}$) is zero. Using eqns. in part II [2] we get C_{noB} from eqn. (9 a) with Z_{noB} from eqn. (12). $Z_{C/B}$ can then be obtained from eqn. (9 c), and c from eqn. (5 a). $Z_{C/B}$ (log $c)_{B,C}$ is shown in Fig. 2.

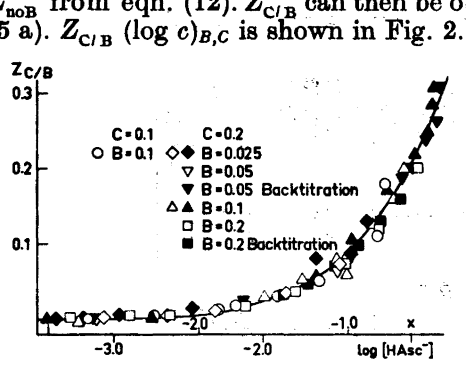

Fig. 2. $Z_{C/B}$ (= the average number of ascorbic acid molecules bound per Cd(II)) as a function of log [$HAsc^-$]. The full curve represents the theoretical curve $[x/(1+x)]$ (log x) for log $\beta_{011} = 0.43$.

As seen in Fig. 2, $Z_{C/B}$ is independent of B. From. eqn. (6 a) we can see that $Z_{C/B}$ is independent of B, if $q = 1$.

$$Z_{C/B} = \sum r\beta_{0qr}\, b^q c^r / (b + \sum \beta_{0qr}\, b^q c^r) \qquad (6\ a)$$

The experimental points of $Z_{C/B}$ could be fitted by a normalized function, assuming a single complex BC (Fig. 2):

$$[x/(1+x)](\log x);\ x=\beta_{011}c \qquad (6\ b)$$

gave $\log \beta_{011}=0.43\pm0.10$

and LETAGROP [9,10] calculations, minimizing $U_H=\sum(H_{calc}-H)^2$ gave

$$\log \beta_{101}=4.373\pm0.005$$
$$\log \beta_{011}=0.44\pm0.04 \qquad (6\ c)$$

138 points were used, giving $\sigma(H)=0.89$ mM, which corresponds to a 0.4 % error in H. Using LETAGROP, we tried to add other complexes, *viz.* BC_2, B_2C, B_2C_2, BHC, BHC_2, and B_2HC_2, but none of these could improve the fit significantly. We introduced H_2C_2 and HC_2^- indicated by our data at higher C values (part I [1]), but β_{011} came out with the same values as before (6 c), and the formation constants for the dimeric species came out as zero within the limits of error (3σ).

The value of $\log \beta_{101}$ agrees well with that found in part I,[1] *viz.* 4.359 ± 0.006. The amount of dimeric species in our solutions with $C\leq0.2$ M is sufficiently small to be neglected in this study.

Graphical treatment of data in the range $-8.7\leq \log h\leq -5.0$

1. *Limiting values of* $Z'_{H/B}$. We consider titrations with $C=0.2$ M, and $B=0.01$, 0.025, 0.05, and 0.1 M (Fig. 1). $Z'_{H/B}$ = the average number of H^+ bound per B in the complexes $H_pB_qC_r$ with q and $r\neq0$ were calculated from: $Z'_{H/B}=(H-h+K_wh^{-1}-B_{noC}Z_{noC}-C_{noB}Z_{noB})/C$ (*cf.* eqns. (9 a–b) in part II [2]). In our solutions $[OH^-]=K_wh^{-1}\approx0$ and $\sum[Cd_q(OH)_n]=B_{noC}Z_{noC}\approx0$. The amount of Asc^{2-} is negligible, and H_2Asc is small. We can approximate $C_{noB}Z_{noB}=[H_2Asc]$ with $C\,Z_{noB}$ and calculate Z_{noB} from eqn. (12) in part II.[2] We thus obtain

$$Z'_{H/B}=(H-h-C\,Z_{noB})/C \text{ (Fig. 3)} \qquad (7\ a)$$

The error introduced by the approximation $C_{noB}\approx C$ is small – less than 0.005 in $Z'_{H/B}$ at $\log h<-7$.

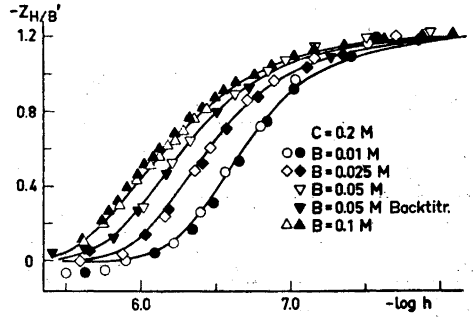

Fig. 3. $Z'_{H/B}$ (= the average number of H^+ bound per Cd(II) in complexes with ascorbic acid) as a function of $\log h$. The full curves have been calculated using HALTAFALL [18] and the final set of complexes.

As seen in Fig. 3, the curves are approximately parallel. A plateau is formed at $Z'_{H/B} = -1.2 \pm 0.1$. The simplest explanation of this phenomenon is that only one predominating complex (PQR) exist at $Z'_{H/B} = -1.2$, and that for this complex $P/Q = -1.2 \pm 0.1$ (*cf.* eqns. (7 a–b) and (8 b) in part II[2]). The possible complexes are then

$$(\bar{5}4R),\ (\bar{6}5R),\ (\bar{7}6R) \text{ and } (PQR) \qquad (7\ b)$$

with a higher Q-value.

The value -1.33 required for $(\bar{4}3R)$ seems too low and the value -1.00 required for $(\bar{1}1R)$, $(\bar{2}2R)$, $(\bar{3}3R)$, $(\bar{4}4R)$, *etc.*, seems too high. More than one complex may of course be present.

2. *Estimation of the mean values $\bar{p}$ and $\bar{q}$.* In solutions with $C = 0.2$ M and small values of B we know that most of the ascorbic acid is present as $C = [HAsc^-]$ when $-8.7 < \log h \leq -5.5$. If $C \gg B$, we can use the self medium principle[2] studying formally B_qH_p, with C in the medium. For $B = 0.01$, 0.025, and 0.05 M $C/B = 20$, 8, and 4, respectively, which may be large enough to try a rough estimation of $\bar{p}$ and $\bar{q}$ by methods used for two component systems.

The $Z'_{H/B}$ curves were calculated as in the previous section. They do not coincide (Fig. 3). This indicates complexes with $q > 1$. We used the MESAK[7] method to estimate $\bar{p}$ and $\bar{q}$ from the lowest B – values. As seen in Table 2, these calculations would suggest an average composition

$$(Cd^{2+})_{3.5 \pm 1}\ (H^+)_{-3.5 \pm 1}\ (HAsc^-)_{\bar{r}}\ .$$

Table 2. The average composition of the complexes $H_pB_qC_r$ with $p < 0$, estimated by the MESAK[7] method for $B = 0.025$, and $C = 0.1$ M.

$Z_{H/B}$	$-\log h$	$\bar{q}$	$\bar{p}$	$Z_{H/B}$	$-\log h$	$\bar{p}$	$\bar{q}$
0.1	6.01	−3.8	3.4	0.5	6.42	−3.4	3.1
0.2	6.12	−3.9	3.5	0.6	6.52	−3.4	3.1
0.3	6.22	−3.4	3.3	0.7	6.63	−3.3	3.1
0.4	6.33	−3.4	3.1	0.8	6.73	−3.3	3.0

3. *$Z_{C/B}$ curves and r-values.* Data with $B = 0.025$ M, and $C = 0.05$, 0.1, and 0.2 M (Fig. 4 a) were used to calculate $Z_{C/B}$ = the average number of C bound per B in $H_pB_qC_r$ with $q \neq 0$ (eqn. (11), part II[2]). We performed the graphical integration as described in Ref. 8. In order to get $Z_{C/B}$ for the basic complexes (those with $p < 0$), we include [BC] in C_{noB}. As one can see in Fig. 4 b, $Z_{C/B}$ and $-Z'_{H/B}$ are approximately equal for $B = 0.025$ M and $C = 0.1$ M. If the complexes could be written $B_q(H\bar{1}C)_p$, or in other terms Cd_qAsc_r, then $Z_{C/B}$ and $-Z'_{H/B}$ would be exactly equal (*cf.* eqns. (7 a–c) and (8 b–c) in part II[2]). For the main species we may conclude that $r \approx -p$.

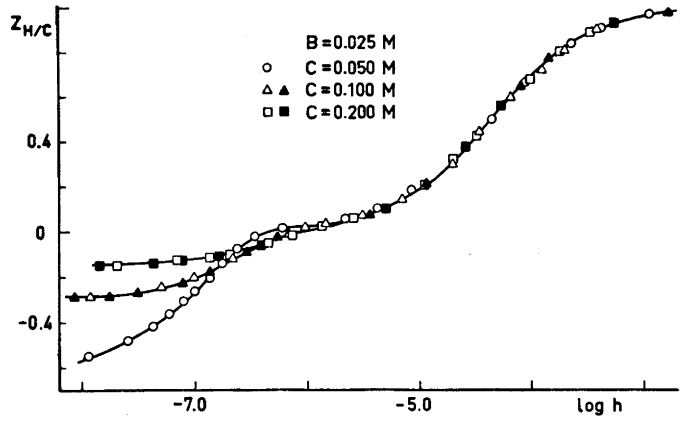

Fig. 4 a. Z ($=Z_{H/C}=$the average number of H^+ bound per $HAsc^-$) as a function of log h. The data used for the graphical integration calculating $Z_{C/B}$ in Fig. 4 b.

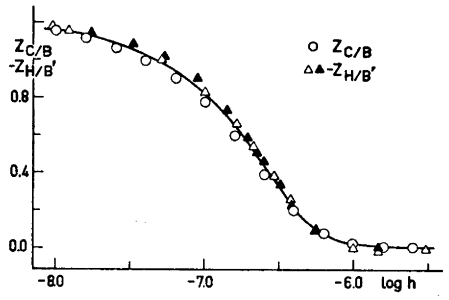

Fig. 4 b. $Z_{H/B}$ and $Z_{C/B}$ as functions of log h. $Z_{C/B}$ has been obtained by graphical integration, using data shown in Fig. 4 a.

Selection of a set of complexes, giving the "best" fit with the data using LETAGROP

We used the information from the graphical treatment, thus starting to test complex combinations containing four complexes: $(101)+(011)+(\bar{5}4R_1)$, $(\bar{6}5R_1)$ or $(\bar{7}6R_1)+(P_2,Q_2,R_2)$ choosing $r-1\leq -p\leq r+1$.

To speed up the calculations we used only a part of the data to select a model. At first 6 titrations with high C-values were picked out and $U_H=\sum(H_{calc}-H)^2$ was minimized, giving high weight to complexes with large r-values (Table 3). The "best" fit was obtained by:

$$(101)+(011)+(\bar{3}34)+(\bar{4}44)+(\bar{6}56); \quad \sigma(H)=0.69 \text{ mM} \qquad (8\text{ a})$$

Other combinations giving good fits are shown in Table 3 a. Rejected complexes are shown in Table 3 c. (Those with $\beta_{pqr}<3\sigma(\beta_{pqr})$.)

To select the final set of complexes we picked out every fifth point and minimized $U_Z=\sum(Z_{calc}-Z)^2$, thus giving equal weight to all points. We tested the combinations given in Table 3 and noted deviations at low values of B and C, corresponding to more basic complexes. Thus $(\bar{2}11)$, $(\bar{2}12)$, $(\bar{3}22)$,

Table 3. LETAGROP calculations, using 138 points with $C = 0.200$ M, and $B = 0.01$, 0.025, 0.05, 0.1, and 0.2 M. $-1 < Z < 1$, $-3 < \log h < -8$, $-0.200 < H \leq 0.250$M. $U_H = \sum (H_{calc} - H)^2$. The complexes are sorted with the more basic ones to the right. The "best" fit model is given in italics. $\log \beta_{101} = 4.37$, and $\log \beta_{011} = 0.43$ were not varied.

	U_H	$\sigma(H)$ (mM)	$(\bar{3}34)$	$(\bar{3}33)$	$\log (\beta_{pqr} \pm 3\sigma)$ $(\bar{4}44)$	Additional complex	
a.	206	1.23		-13.20 ± 0.07		-19.25 ± 0.14 $(\bar{4}34)$	
	145	1.07		-13.28 ± 0.07		-22.90 ± 0.10 $(\bar{5}45)$	
	137	1.05		-13.30 ± 0.08		-30.30 ± 0.08 $(\bar{7}67)$	
	120	0.99	-12.53 ± 0.08			-26.39 ± 0.05 $(\bar{6}56)$	
	96	0.84			-17.17 ± 0.07	-22.92 ± 0.10 $(\bar{5}45)$	
	83	0.79		-13.35 ± 0.08		-26.65 ± 0.08 $(\bar{6}56)$	
	82	0.78		-13.43 ± 0.3	-17.99 ± 0.4	-26.66 ± 0.09 $(\bar{6}56)$	
	78	0.76	-12.76 ± 0.19	-13.47 ± 0.17		-26.55 ± 0.12 $(\bar{6}56)$	
	69	*0.69*	-12.98 ± 0.3		-17.40 ± 0.15	-26.54 ± 0.10 $(\bar{6}56)$	
b.	89	0.81	-12.86 ± 0.3			-26.34 ± 0.06 $(\bar{6}56)$	-20.08 ± 0.21 $(\bar{5}56)$
	77	0.76			-17.46 ± 0.23	-26.51 ± 0.12 $(\bar{6}56)$	-20.38 ± 0.26 $(\bar{5}56)$
	72	0.73		-13.54 ± 0.20		-26.52 ± 0.11 $(\bar{6}56)$	-20.50 ± 0.24 $(\bar{5}56)$

c. Rejected complexes ($\beta < 3\sigma(\beta)$)

PQR	log β max	*PQR*	log β max	*PQR*	log β max
$\bar{7}67$	-30.4	$\bar{2}33$	-9.2	$\bar{2}12$	-13.0
$\bar{5}45$	-22.2	$\bar{2}32$	-16.4	$\bar{2}11$	-13.7
$\bar{4}43$	-19.4	$\bar{3}23$	-17.5	$\bar{1}12$	-5.5
$\bar{3}44$	-11.1	$\bar{2}23$	-9.2	$\bar{1}11$	-6.4
$\bar{3}43$	-12.7	$\bar{2}22$	-9.9		
$\bar{4}34$	-20.0	$\bar{2}21$	-12.7		
$\bar{4}33$	-19.7	$\bar{1}22$	-4.5		
$\bar{3}32$	-15.5	$\bar{1}21$	-5.2		

($\bar{3}23$), ($\bar{4}33$), ($\bar{5}44$), and ($\bar{6}55$) were tried. Combinations giving low $\sigma(Z)$ and U-values are shown in Table 4. The "best" fit was obtained by:

$$(101)+(011)+(\bar{3}33)+(\bar{3}34)+(\bar{4}33)+(\bar{6}56);\ \sigma(Z)=0.0097 \qquad (8\ b)$$

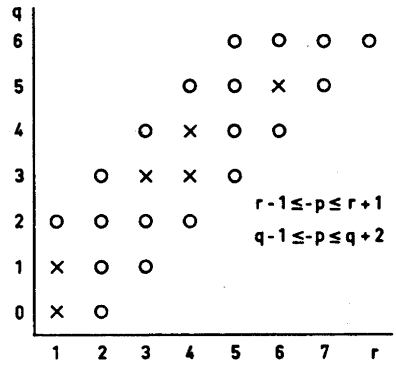

Fig. 5. Complexes tested by LETAGROP, using every fifth point in all titrations. (q,r) for complexes given as the final result are marked with ×.

Many complexes were now tried, using the "SPECIES SELECTOR" in LETAGROP [10] (Fig. 5). We found that if ($\bar{3}34$) was exchanged to ($\bar{5}56$), a better fit was obtained. The "best" fit with the data was obtained by:

$$(101)+(011)+(\bar{3}33)+(\bar{4}33)+(\bar{5}56)+(\bar{6}56);\quad \sigma(Z)=0.0095 \qquad (8\ c)$$

All other complexes were rejected. For these, $\beta_{pqr} < 3\sigma(\beta_{pqr})$. As seen in Table 4, combinations containing ($\bar{3}34$) and ($\bar{4}44$) also give low $\sigma(Z)$-values, but not as low as the final model (8 c).

Refinement of the model by least squares treatment (LETAGROP)

The final set of complexes (8 c) was refined, minimizing $U_Z = \sum(Z_{calc}-Z)^2$, using all 559 points (Table 5). The 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 $E_0=E_0$ (calculated from a few acid points, *cf.* part II [2]) $+\delta E_0$
Final $H=H$ (calculated from analyses) $+\delta H$ (9)

To save computer time, we used "the first strategy" in Ref. 9 (*cf.* part I [1]). After 3 cycles, log β_{pqr} changed less than 3σ, the variation of U_Z was less than 1 %, and the systematic errors changed about 10 % (*cf.* Table 1 b).

δE_0 and δH are of the expected magnitude (Table 1 b). The corresponding errors δ log h and δZ are small and have no trends. They correspond to very small shifts of the curves Z (log $h)_{B,C}$ in Fig. 1. We tested for an acid impurity, but its concentration came out less than 0.05 mM, when $C=5$ mM. We used HALTAFALL,[13] and Biedermann and Ciavatta's constants, to calculate that less than 0.1 % of Cd(II) was present on $Cd_q(OH)_n$.

The final value, $\sigma(Z)=0.0063$ for $-1<Z\leq 1$, is very good.

Table 4. LETAGROP calculations, using 119 points from all titrations. $U_Z = \sum (Z_{calc} - Z)^2$. hydrolysis constants were included but not varied (log $\beta_{\bar{1}10} = -10.2$, log $\beta_{\bar{1}20} = -9.2$, and the most basic ones are found to the right.

$U_Z \times 10^3$	$\sigma(Z)$	$P/R = 1.0$	$P/R = 0$	$-1.0 < P/R < 0$	
		$P = 1$			
		$Q = 0$	$P/Q = 0$	$P/Q = -1.0$	
		(101)	(011)	($\bar{3}34$)	($\bar{5}56$)
165	0.0119	4.372 n.v.	0.42 n.v.		
142	0.0111	»	»	-12.41 ± 0.15	
142	0.0111	»	»		
141	0.0111	»	»		
140	0.0111	»	»		
139	0.0109	»	»		
135	0.0107	»	»		
135	0.0107	»	»		
131	0.0106	»	»		-20.41 ± 0.3
127	0.0105	»	»	-12.39 ± 0.14	
127	0.0105	»	»		
127	0.0105	»	»		
123	0.0103	»	»		
113	0.0099	»	»		-20.33 ± 0.3
110	0.0098	»	»	-12.77 ± 0.3	
107	0.0097	»	»	-12.69 ± 0.3	
107	0.0097	»	»	-12.69 ± 0.3	
106	0.0095	»	»		-20.36 ± 0.25
104	*0.0094*	»	»		*-20.33 ± 0.22*

RESULTS AND DISCUSSION

As the final result we propose the following reactions and constants valid in 3 M $NaClO_4$ medium at 25°C:

pqr	Reaction	log ($\beta_{pqr} \pm 3\sigma$)	
1. 101	$HAsc^- + H^+ \rightleftharpoons H_2Asc$	4.371 ± 0.005	
2. 011	$Cd^{2+} + HAsc^- \rightleftharpoons CdHAsc^+$	0.42 ± 0.05	
3. $\bar{3}33$	$3\ Cd^{2+} + 3\ HAsc^- \rightleftharpoons Cd_3Asc_3 + 3\ H^+$	-13.65 ± 0.05	
4. $\bar{4}33$	$3\ Cd^{2+} + 3\ HAsc^- \rightleftharpoons Cd_3Asc_3OH^- + 4\ H^+$	-21.14 ± 0.02	(10)
5. $\bar{5}56$	$5\ Cd^{2+} + 6\ HAsc^- \rightleftharpoons Cd_5Asc_6H^- + 5\ H^+$	-20.42 ± 0.12	
6. $\bar{6}56$	$5\ Cd^{2+} + 6\ HAsc^- \rightleftharpoons Cd_5Asc_6^{2-} + 6\ H^+$	-26.57 ± 0.06	

Table 5. Results from LETAGROP calculations, using all 559 points minimizing $U_Z = \sum (Z_{calc} - Z)^2$. The systematic errors are shown in Table 1 b. The corresponding reactions are given in eqn. (10). (Refinement.)

$U_Z \cdot 10^3$	$\sigma(Z)$	log $\beta_{pqr}(pqr)$		
21.6	0.0063	4.371 ± 0.005 (101)	0.42 ± 0.05 (011)	-13.65 ± 0.05 ($\bar{3}33$)
		-21.14 ± 0.02 (433)	-20.42 ± 0.12 ($\bar{5}56$)	-26.57 ± 0.06 ($\bar{6}56$)

Selection of a final model (n.v. = not varied). Log ($\beta_{pqr} \pm 3\sigma$) is given. Biedermann and Ciavatta's log $\beta_{\bar{4}40} = -31.8$). Systematic errors assumed to be zero. The complexes $H_pB_qC_r$ are sorted, so that The model giving "best fit" is given in italics.

$P/R = -1.0$					$P/R < -1.0$	
$P/Q = -1.0$		$-1.3 < P/Q < -1.0$			$P/Q < -1.3$	
($\bar{3}33$)	($\bar{4}44$)	($\bar{5}45$)	($\bar{6}56$)	($\bar{7}67$)	($\bar{3}22$)	($\bar{4}33$)
-13.52 ± 0.14				-30.21 ± 0.20		
			-26.51 ± 0.15		18.02 ± 0.08	
-13.44 ± 0.10		-22.84 ± 0.17				-21.30 ± 0.12
	-17.30 ± 0.13				18.00 ± 0.08	
-13.51 ± 0.13				-30.30 ± 0.21		-21.19 ± 0.10
-13.45 ± 0.11		-22.78 ± 0.15			-18.13 ± 0.12	
-13.51 ± 0.12			-26.47 ± 0.15		-18.04 ± 0.07	
	-17.25 ± 0.11	-22.89 ± 0.19				-21.22 ± 0.11
	-17.59 ± 0.2		-26.44 ± 0.15		-18.00 ± 0.08	
			-26.32 ± 0.12			-21.18 ± 0.09
-13.49 ± 0.11			-26.56 ± 0.18			-21.23 ± 0.10
	-17.28 ± 0.12		-26.61 ± 0.19			-21.17 ± 0.09
-13.85 ± 0.4	-17.61 ± 0.4		-26.59 ± 0.17			-21.20 ± 0.09
	-17.51 ± 0.3		-26.54 ± 0.17			-21.17 ± 0.09
	-17.48 ± 0.3		-26.54 ± 0.16			-21.16 ± 0.07
-13.70 ± 0.22			-26.50 ± 0.13			-21.20 ± 0.09
-13.87 ± 0.22	-18.00 n.v.		-26.50 ± 0.26			-21.10 ± 0.09
-13.82 ± 0.22	-18.00 n.v.		-26.54 ± 0.17			-21.18 ± 0.09
-13.70 ± 0.22			*-26.52 ± 0.16*			*-21.19 ± 0.09*

We also got evidence for Cd_4Asc_4 and $Cd_3Asc_4H^-$. Below are given reactions with log $\beta_{pqr} \pm$ (maximum limit of error):

7. $\bar{4}44$ 4 $Cd^{2+} + 4$ $HAsc^- \rightleftharpoons Cd_4Asc_4 + 4$ H^+ $\quad -17.5 \pm 0.5$
8. $\bar{3}34$ 3 $Cd^{2+} + 3$ $HAsc^- \rightleftharpoons Cd_3Asc_3H^- + 3$ H^+ $\quad -12.5 \pm 0.5$

Thus, in acid solutions, where $-5.0 \leq \log h \leq -1.3$, we have found that H_2Asc, $HAsc^-$, $CdHAsc^+$ are predominating. In neutral solutions, where $-8.7 \leq \log h \leq -5.0$, the main species are $HAsc^-$, $CdHAsc^+$, Cd_3Asc_3, $Cd_5Asc_6^{2-}$ and two ions formed from these species by reactions with H^+, *viz.* $Cd_3Asc_3OH^-$ and $Cd_5Asc_6H^-$. The distribution of ascorbic acid on different species is shown in Fig. 6.

Cd_4Asc_4 is probably important at high concentrations of cadmium (B) or ascorbic acid (C). In solutions with $C \gg B$, Cd_3Asc_4 H^- may predominate over $Cd_5Asc_6H^-$.

It should be noted that, from our data, we cannot get information about the amount of H_2O, Na^+, and ClO_4^- in the complex species. We do not know the structure of the complexes. For these reasons, we may write the species in different ways. For example, ($\bar{5}56$) may be written as $Cd_5Asc_5HAsc^-$, $Cd_5(HAsc)_6(OH)_5^-$, or $Cd_5Asc_6H^-$, *etc.* To get some idea about the architecture of the complexes, it would be interesting to know the crystal structure of solid cadmium ascorbate.

Veselinović and Sušić [14] have also found that $CdHAsc^+$ predominates in acid solutions (log $\beta_{101} = 1.3$).

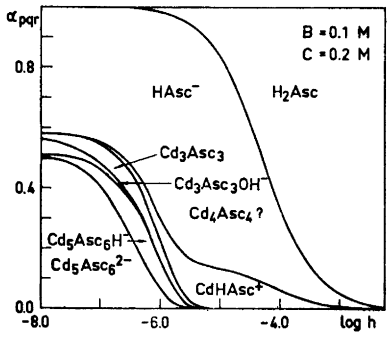

Fig. 6 a. Distribution diagram for ascorbic acid, calculated using HALTAFALL.[13] At a given value of log h, the fraction of ascorbic acid present as $H_pB_qC_r$ is represented by the segment of a vertical line falling within the corresponding area.

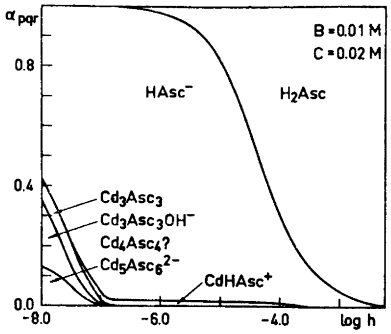

Fig. 6 b. Distribution diagram for asorbic acid, calculated using HALTAFALL.[13]

APPENDIX

The complex formation treated as equilibria between Cd^{2+} and Asc^{2-}, "core and links" treatment [15-17] (in the region $-8.0 \leq \log [H^+] \leq -6.0$)

If we assume, for the complexes $H_pB_qC_r$, that $-p = r$, and that the weak complex $CdHAsc^+$ can be neglected, it is possible to calculate the average number of Asc^{2-} bound to one $Cd^{2+} = Z^*_{C/B}$ and $[Asc^{2-}]$ from eqns. (11 a-b), as shown in part II[2] of Ref. 15, p. 59.

$$Z^*_{C/B} = C - (H - h + K_w h^{-1})/Z^*_{noB} \quad (11\ a)$$

$$[Asc^{2-}] = (H - h + K_w h^{-1})/(\beta^*_{11} h + 2\beta^*_{21} h^2) \quad (11\ b)$$

where $$Z^*_{noB} = (\beta^*_{11} h + 2\beta^*_{21} h^2)/(1 + \beta^*_{11} h + \beta^*_{21} h^2) \quad (11\ c)$$

β^*_{11} and β^*_{21} are defined by $[HAsc^-] = \beta^*_{11}[Asc^{2-}]h$ and $[H_2Asc[= \beta^*_{21}]Asc^{2-}]h^2$ (11 d)

$Z^*_{C/B}$ (log $[Asc^{2-}])_{B,C}$ is a family of parallel curves (Fig. 7 a). If we transform $Z^*_{C/B}$ to $y(x)_C$ by $y = Z^*_{C/B}/1.5$ and $x = \log B + 1.5 \log [Asc^{2-}]$, the parallel curves merge to one single curve $y(x)_C$ (Fig. 7 b). This implies that the complexes are members of the series $B(C_tB)_N$, where $t = d \log B/d \log [Asc^{2-}]$ ($t = 1.5$).

The equilibria can be written

$$(N+1)\,B + 1.5\,N\,C \rightleftharpoons B(C_{1.5}B)_N \quad (12\ a)$$

The law of mass action gives

$$[B(C_{1.5}B)_N] = K_N{}^N b u^N, \text{ where } u = bc^{1.5} \quad (12\ b)$$

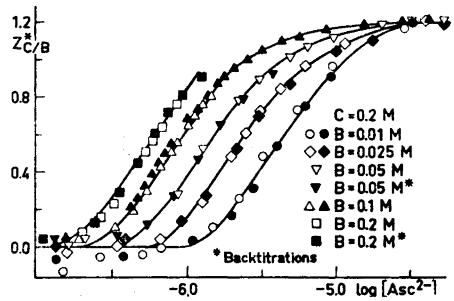

Fig. 7 a. $Z^*_{C/B}$ (= the average number of Asc^{2-} bound per Cd^{2+}) as a function of log [Asc^{2-}].

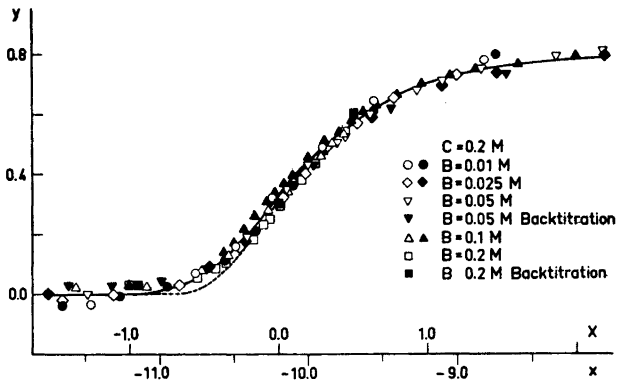

Fig. 7 b. $y(x)$, where $y = Z^*_{C/B}/1.5$ and $x = \log B + 1.5 \log [Asc^{2-}]$. The full curve corresponds to $Cd_3Asc_3 + Cd_5Asc_6^{2-}$, and the dotted curve to $Cd_5Asc_6^{2-}$.

Normalized curves, assuming $N = 2$ and $N = 4$, were calculated, corresponding to single complexes B_3C_3 and B_5C_6, respectively. The experimental points of $y(x)_C$ were well fitted by one theoretical curve $y(X)$, assuming the formation of only B_5C_6, but the fit was improved assuming both B_3C_3 and B_5C_6 (Fig. 7 b).

Calculation of theoretical curves. Estimation of $\beta_{\bar{3}\bar{3}3}$ and $\beta_{\bar{6}\bar{5}6}$

Assuming $N = 4$:

$$y = 4\,g/(1+5\,g);\; X = 1/4 \log g + \log(1+5\,g) + \log 2 - 1/4 \log g_{\frac{1}{2}} - \log(1+5\,g_{\frac{1}{2}}) \qquad (13)$$

where $g_{\frac{1}{2}}$ is the value of g that makes $y = 1/2$
Assuming $N = 2$ and $N = 4$:

$$y = (2RW + 4W^2)/(1 + 3RW + 5W^2)$$
$$X = \tfrac{1}{2} \log W + \log(1 + 3RW + 5W^2) + \log 2 - \tfrac{1}{2} \log W_{\frac{1}{2}} - \log(1 + 3\,RW_{\frac{1}{2}} + 5W_{\frac{1}{2}}^2) \qquad (14)$$

where $W_{\frac{1}{2}}$ is the value that makes $y = 1/2$
g, W, and R are defined by: $g = K_N{}^N u^N$, $W = K_4{}^2 u^2$, and $R = K_2{}^2 K_4{}^{-2}$
From the "best" fit we get (Fig. 7 b):

$$\tfrac{1}{2} \log R = \log K_2 - \log K_4 = -0.30$$
and
$$X - x + x_C = \log K_4 = 10.25$$

where $x_C = \frac{1}{2} \log W_{\frac{1}{2}} + \log (1 + 3RW_{\frac{1}{2}} + 5W_{\frac{1}{2}}{}^2) - \log 2$

This gives $\log K_2 = 9.95$, and $\log K_4 = 10.25$. From these values we can calculate $\beta_{\bar{3}\bar{3}3}$ and $\beta_{\bar{6}\bar{5}6}$ using $\log \beta_{11}{}^* = 11.34$ (*cf.* part I[1]):

$$\begin{aligned} \log \beta_{\bar{3}\bar{3}3} &= 2 \log K_2 - 3 \log \beta_{11}{}^* = -14.1 \pm 0.5 \\ \log \beta_{\bar{6}\bar{5}6} &= 4 \log K_4 - 6 \log \beta_{11}{}^* = -27.0 \pm 0.5 \end{aligned} \qquad (15)$$

Other C-values give slightly different constants. This "two parameter approximation" of the complex formation agrees well with the equilibrium model found in the previous sections.

Since, in the appendix, we have started by introducing two limiting assumptions, we think it is reasonable only to compare the experimental data with two normalized curves leaving out calculation of the average number of composite ligands bound to one B by direct analysis of $y(x)$.

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