Equilibrium Studies of L-Ascorbate Ions

V. Cadmium Ascorbate Complexes in Self Media Containing 3 M (Na,Cd)ClO₄ and Ascorbic Acid

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By potentiometric titrations using glass electrodes at 25°C we obtained 185 experimental points. Concentration ranges used: 0.4 M ≤ [Cd²⁺]tot ≤ 1.4 M, 0.4 ≤ [HAsc]tot ≤ 1.0 M and -3.4 ≤ log[H⁺] ≤ -0.8, where HAsc = ascorbic acid.

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

The predominating species seem to be HAsc, HAsc⁻, HAAsc₂⁺, HAAsc⁻, and CdHAAsc⁺. We also found evidence for Cd₂HAAsc₂⁺.

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

In parts III³ and IV⁴ of this series we have studied the system Cd²⁺ – HAsc⁻ – H⁺ at lower ascorbic acid concentrations (C ≤ 0.2 M). We found that in acid solutions, where HAsc⁻ is important, the predominating cadmium complex is CdHAAsc⁺ even in solutions where B/C = 40 or C/B = 20. In the present investigation we have studied complexes Cdₓ(HAsc)Hₓ in solutions with B ≥ 0.4 M and C ≥ 0.4 M. To keep the activity coefficients constant we restricted the Z-values to 0.85 ≤ Z ≤ 1.0.

The equilibria treated in this article can be written

\[ p\text{H}^+ (h) + q \text{Cd}^{2+} (b) + r \text{C} (c) \rightleftharpoons \text{H}_p \text{B}_q \text{C}_r (c_{pr}) \]  \hspace{1cm} (1)

SYMBOLS

The reactant symbols H, B, and C stand for H⁺, Cd²⁺, and ascorbic acid. Total concentrations are written H, B, C, and free concentrations h, b, c. H is the excess (analytical) concentration of H⁺ over Cd²⁺, H₂O, and C. For convenience we have chosen C = H₂Asc in the graphical treatment. In the

LETAGROP\textsuperscript{7,8} calculation, however, we use $C = HAsc^-$, as we did in parts III\textsuperscript{3} and IV\textsuperscript{4} of this series.

$Z$, the average number of $H^+$ bound per $C$, $C_{\text{on}} = [HAsc] + [HAsc^-] + 2[HAsc_2] + 2[HAsc_2^-]$. $(V,E)$ = volume and emf measured. A complete list of symbols is given in part II\textsuperscript{2}.

**EXPERIMENTAL**

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

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

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

![Graph](image)

**Fig. 1.** $Z_{H,C}$ (= the average number of $H^+$ bound per $C$) as a function of $\log h$. The solid curves were calculated, using HALTA-FALL\textsuperscript{4} and constants from eqn. (14). Filled symbols = back titrations.

**SURVEY OF EXPERIMENTAL DATA**

For each titration we have calculated $E_0$ and corrected $H_0$ or $H_T$ using the computer program TRAVE\textsuperscript{5} as described in part II\textsuperscript{2}.

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

Table 1a. Experimental data (computer output from LETAGROP). For each point in a titration ("S" data) are given V—the volume of the buret solution with total concentrations \( H^+ \), \( B_r \), and \( C_{r'} \) added to \( V_p \) ml of a solution with total concentrations \( H_p \), \( B_p \), and \( C_{p'} \) E ("EA") \log [H\(^+\)] ("LOGA") \( H ("ATOT") \) and \( H_{calc} ("DATOT") \). \( H_{calc} \) was calculated using the equilibrium constants in Table 3.

The systematic errors \( \delta H \) and the final values of \( E_p \) are given in Table 1b.

### Table 1a

<table>
<thead>
<tr>
<th>( E_p )</th>
<th>( H_p )</th>
<th>( B_p )</th>
<th>( C_{p'} )</th>
<th>( E_A )</th>
<th>( \log [H^+] )</th>
<th>( H )</th>
<th>( H_{calc} )</th>
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<td>( V ) (ml)</td>
<td>( \Delta V ) (ml)</td>
<td>( \Delta H ) (mm)</td>
<td>( \Delta \log [H^+] ) (mm)</td>
<td>( \Delta H ) (mm)</td>
<td>( \Delta \log [H^+] ) (mm)</td>
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<th>( \Delta H ) (mm)</th>
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### Table 1g

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<th>( \Delta H ) (mm)</th>
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<th>( \Delta H ) (mm)</th>
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### Table 1h

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<th>( \Delta H ) (mm)</th>
<th>( \Delta \log [H^+] ) (mm)</th>
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Table 1b. For each titration are given: the total concentrations, $E_0$, estimated from a few acid points, the final value of $E_0$, $j$, and $\delta H$ obtained in the refinement of the equilibrium model (from LETAGROP). Concentrations are in M, and emf values in mV.

<table>
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<tr>
<th>Titration No.</th>
<th>$B$</th>
<th>$C$</th>
<th>$H_0$ (from acid points)</th>
<th>$E_0$</th>
<th>$E_0 \pm 3\sigma$ (refined)</th>
<th>$j \pm 3\sigma$</th>
<th>$10^4(\delta H \pm 3\sigma)$</th>
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<td>1</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5028</td>
<td>0.1512</td>
<td>355.3</td>
<td>$-17.5 \pm 1.8$</td>
<td>$0.7 \pm 0.4$</td>
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<td>2</td>
<td>0.4</td>
<td>0.7</td>
<td>0.8266</td>
<td>0.2004</td>
<td>363.9</td>
<td>$-17.4 \pm 0.5$</td>
<td>$0.8 \pm 0.6$</td>
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<tr>
<td>3</td>
<td>0.4</td>
<td>0.7</td>
<td>0.5956</td>
<td>1.0870</td>
<td>363.6</td>
<td>$-17.4 \pm 0.5$</td>
<td>$-0.9 \pm 0.6$</td>
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<tr>
<td>4</td>
<td>0.4</td>
<td>1.0</td>
<td>0.8550</td>
<td>1.4831</td>
<td>374.7</td>
<td>$-17.7 \pm 0.4$</td>
<td>$-1.3 \pm 1.2$</td>
</tr>
<tr>
<td>5</td>
<td>0.7</td>
<td>1.0</td>
<td>1.1649</td>
<td>0.6031</td>
<td>379.8</td>
<td>$-17.5 \pm 0.6$</td>
<td>$-2.7 \pm 0.8$</td>
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<tr>
<td>6</td>
<td>1.2</td>
<td>1.0</td>
<td>1.1645</td>
<td>0.4075</td>
<td>381.4</td>
<td>$-17.5 \pm 0.9$</td>
<td>$-4.4 \pm 1.1$</td>
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<td>7</td>
<td>1.4</td>
<td>1.0</td>
<td>1.1634</td>
<td>0.6068</td>
<td>382.7</td>
<td>$-18.3 \pm 1.1$</td>
<td>$-4.9 \pm 2.4$</td>
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</table>

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

\[ E = E_0 + 59.155 \log h + E_j \]
\[ j = -17 \text{ h} \quad (2) \]

\[ H = (V_0 H_0 + V H_T)/(V_0 + V) \]
\[ B = B_0 = B_T \quad (3 \ a) \]

\[ C = C_0 = C_T \quad (3 \ b) \]

\[ Z = (H - h + K_w h^{1/2})/C \quad (4) \]

\[ H = h + \sum p \beta_{pq} h^p b^q c^r \quad (5 \ a) \]

\[ B = b + \sum q \beta_{pq} h^p b^q c^r \quad (5 \ b) \]

\[ C = c + \sum r \beta_{pq} h^p b^q c^r \quad (5 \ c) \]

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

**TREATMENT OF DATA**

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

In the graphical treatment we have chosen $\text{H}_2\text{Asc}$, $\text{H}^+$ and $\text{Cd}^{2+}$ as components. This is practical, since $\text{Cd}^{2+}$, $\text{H}_2\text{Asc}$, and $\text{H}_4\text{Asc}_2$ are present in high and constant concentrations.

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

**Graphical treatment**

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

\[ H - h = \sum p c_{pqr} \tag{6 a} \]
\[ c_{pqr} = K_b^p h^p \tag{6 b} \]
\[ K_p = \sum \beta_{pqr} b^q c^r \tag{6 c} \]

where \( b \) and \( c \) are approximately constant.

1. **Determination of \( \bar{p} \):** the average value of \( p \) in the complexes. By definition
\[
\bar{p} = \frac{\sum p c_{pqr}}{\sum c_{pqr}} \tag{7}
\]
Differentiation of (6 b) and insertion of (6 a) followed by integration gives
\[
\sum c_{pqr} = \int_{\log h}^{\log h} (H - h) d\log h \tag{8}
\]
Eqns. (6 a), (7) and (8) give:
\[
\bar{p} = (H - h) \left( \int_{\log h}^{\log h} (H - h) d\log h \right) \tag{9}
\]
From eqn. (9) \( \bar{p} \) was calculated by graphical integration using the trapezoid formula. The result is shown in Fig. 2:
\[
\bar{p} = -1.0 \pm 0.2
\]

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

**Fig. 3.** \( \log (h - H) \) as a function of \( \log h \). Filled symbols = back titrations. The solid lines correspond to eqn. (10) with \( K_1 \) from Table 2.

2. **Determination of monoligandic constants \( K_1 \).** From eqns. (6 a – b) we get
\[ h - H = K_1 h^{-1} \ (p = -1) \]
Taking the logarithm gives
\[
\log (h - H) = -\log h + \log K_1 \tag{10}
\]
For constant \( B \) and \( C \), \( \log (h - H) \) as a function of \( \log h \) is a straight line. The slope is \(-1\) and the intercept at \( \log h = 0 \) is \( \log K_1 \) (Fig. 3). From the best fit of lines in Fig. 3 we obtain \( K_1 \) for each pair \((B, C)\). The values of \( K_1 \) are found in Table 2.

Table 2. Analysis of $K_1 = (h - H) h = [\text{HAsc}^-]h + [\text{H}_2\text{Asc}^-]h + \sum [\text{Cd}_q(\text{H}_2\text{Asc})_q H_p] h$. $K'_{1} = \sum [\text{Cd}_q(\text{H}_2\text{Asc})_q H_p] h$. $b \approx B$ and $c = [\text{H}_2\text{Asc}]$ is estimated from eqn. (10).

<table>
<thead>
<tr>
<th>$BM$ $(b \approx B)$</th>
<th>$C M$</th>
<th>$K_1 \times 10^4$</th>
<th>$[\text{H}_2\text{Asc}^-]h \times 10^4$</th>
<th>$[\text{HAsc}^-]h \times 10^4$</th>
<th>$K_1' \times 10^4$</th>
<th>$\beta_{011} = \frac{K_1'}{b \times c} \times \beta_{111}$</th>
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<td>0.4</td>
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<td>0.416</td>
<td>0.190</td>
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<td>0.965</td>
<td>0.540</td>
<td>0.247</td>
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<td>1.622</td>
<td>0.550</td>
<td>0.251</td>
<td>0.178</td>
<td>1.193</td>
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</table>

3. Analysis of $K_1 (b,c)$. From eqn. (6) we get the amount of $H^+$ bound in complexes as

$$H - h = K_1 h^{-1}$$

where $K_1 = \sum \beta_{1qr} b_c r_c$

We approximate $b = B$, and estimate $c = [\text{H}_2\text{Asc}]$ from eqns. (11 a – b).

$$2[\text{H}_2\text{Asc}_2] + [\text{H}_2\text{Asc}] = C$$

(11 a)

$$[\text{H}_2\text{Asc}_3] = 0.69 [\text{H}_2\text{Asc}]^3$$

(11 b)

Eqn. (11 b) concerns the equilibrium $2\text{H}_2\text{Asc} \rightleftharpoons \text{H}_2\text{Asc}_2$. The constant $= 0.69$ was obtained in part I.\(^1\)

As a first approximation we assume $\text{CdHAsc}^+$ to be the only cadmium complex present in the solution (Table 2). We subtracted the contribution to $H - h$ from $\text{HAsc}^-$ and $\text{H}_2\text{Asc}_q^-$, taking the necessary equilibrium constants from part I.\(^1\) The calculated formation constant for $\text{CdHAsc}^+ = \beta_{011}$ varies a little when $B$ is increased from 0.4 to 1.4, but seems roughly independent of $C$. Because of the approximations introduced and the small variation of $\beta_{011}$ with $B$ it is difficult to say anything about complexes with higher $q$- or $r$-values. The predominant equilibrium for $\text{Cd}(II)$ seems to be

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

Calculations using LETAGROP

Selection of complexes. From the graphical treatment we know that the main $\text{Cd}(II)$ species can be written $\text{Cd}_q(\text{H}_2\text{Asc})_q[H^+]_i$ or $\text{Cd}_q(\text{H}_2\text{Asc})_{q-i}\text{HAsc}$. The pure ascorbic acid species we know from part I.\(^1\) They are (101), (102), and (202). The graphical treatment indicates $\text{CdHAsc}^+$ to be present.

The apparent value of $\beta_{011}$ was now calculated, using LETAGROP\(^7,8\) minimizing $U = (Z_{\text{calc}} - Z)^4$. The primary data $(V,E)_{B,C}$ were used directly without any approximations. Each medium, thus with constant $(B,C)$ was treated separately. As seen in Fig. 4, $\beta_{011}'$ increases with increasing $B$. This can be explained by a model containing the complex $\text{Cd}_q(\text{H}_2\text{Asc})_{q-1}\text{HAsc}$ with $Q > 1$ thus:
1. The value of Q. The amount of C bound in the complexes with cadmium (II) can be written:

\[ C - C_{\text{nob}} = \sum r \beta_{pqr} \ h_{b} c_{c'} \]  

(12 b)

If we introduce \([\text{H}_2\text{Asc}] = \beta_{001} b_c\) and \( b \approx B \) in (12 b) and assume that \( \text{CdHAsc}^+ \) and \( \text{Cd}_3(\text{H}_2\text{Asc})_{8-1}\text{HAsc} \) are present (12 b) can be written:

\[ C - C_{\text{nob}} = r \beta'_{011} B c \]

where

\[ \beta'_{011} = \beta_{011} + \beta_{R-1,0,R} \times \beta_{101}^{-1} \times B^{0-1} \times [\text{H}_2\text{Asc}]^{R-1} \]

In Fig. 4 we have plotted \( \beta'_{011} \) obtained from LETAGROP calculations against \( B \) at constant \( C = 1 \text{ M} \). Since \([\text{H}_2\text{Asc}]\) is a constant, we obtain:

\[ \beta'_{011} = \beta_{011} + \text{const.} \quad B^{0-1} \]  

(12 c)

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

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

\[ \text{Fig. 5. } U_s = \sum (Z_{\text{calc}} - Z)^2 \text{ as a function of } p \text{ and } r, \text{ } q = 2. \]

**Table 3.** Results of LETAGROP calculations, using all points (185), minimizing \( U_s = \sum (Z_{\text{calc}} - Z)^2 \).

<table>
<thead>
<tr>
<th>( U \times 10^4 )</th>
<th>( \delta Z )</th>
<th>( \log (\beta_{pqr} \pm 3\sigma) )</th>
<th>( (pqr) = (101) )</th>
<th>( (102) )</th>
<th>( (202) )</th>
<th>( (011) )</th>
<th>( (122) )</th>
<th>The systematic errors</th>
</tr>
</thead>
<tbody>
<tr>
<td>246</td>
<td>0.0037</td>
<td>4.34 ( \pm ) 0.01</td>
<td>4.45</td>
<td>8.56</td>
<td>0.56 ( \pm ) 0.02</td>
<td>( \delta E_9 = 0, \delta H = 0 )</td>
<td>( \delta E_9 ) and ( \delta H ) adjusted</td>
<td></td>
</tr>
<tr>
<td>109</td>
<td>0.0030</td>
<td>4.34 ( \pm ) 0.01</td>
<td>4.45</td>
<td>8.56</td>
<td>0.56 ( \pm ) 0.01</td>
<td>( \delta E_9 = 0, \delta H = 0 )</td>
<td>( \delta E_9 ) and ( \delta H ) adjusted</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.0018</td>
<td>4.34 ( \pm ) 0.01</td>
<td>4.45</td>
<td>8.56</td>
<td>0.47 ( \pm ) 0.009</td>
<td>4.67 ( \pm ) 0.02</td>
<td>( \delta E_9 = 0, \delta H = 0 )</td>
<td>( \delta E_9 ) and ( \delta H ) adjusted</td>
</tr>
<tr>
<td>30</td>
<td>0.0013</td>
<td>4.34 ( \pm ) 0.01</td>
<td>4.45</td>
<td>8.56</td>
<td>0.47 ( \pm ) 0.008</td>
<td>4.66 ( \pm ) 0.007</td>
<td>( \delta E_9 ) and ( \delta H ) adjusted</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>0.0017</td>
<td>4.34 ( \pm ) 0.01</td>
<td>4.26 ( \pm ) 0.03</td>
<td>8.49 ( \pm ) 0.01</td>
<td>0.49 ( \pm ) 0.005</td>
<td>4.55 ( \pm ) 0.002</td>
<td>( \delta E_9 = 0, \delta H = 0 )</td>
<td>( \delta E_9 ) and ( \delta H ) adjusted</td>
</tr>
<tr>
<td>16</td>
<td>0.0009</td>
<td>4.36 ( \pm ) 0.01</td>
<td>4.28 ( \pm ) 0.09</td>
<td>8.48 ( \pm ) 0.003</td>
<td>0.50 ( \pm ) 0.006</td>
<td>4.66 ( \pm ) 0.002</td>
<td>( \delta E_9 ) and ( \delta H ) adjusted</td>
<td></td>
</tr>
</tbody>
</table>

**Notes.** Values obtained in part I; \( \log \beta_{181} = 4.359 \pm 0.006, \log \beta_{182} = 4.45 \pm 0.04, \) and \( \log \beta_{183} = 8.56 \pm 0.05. \) The equilibrium constants were not varied at the same time as systematic errors were adjusted (cf. part I').

2. The value of R. Determination of $\beta_{fQR}$. To determine the most probable value of $R$ we have calculated $U_i = \Sigma (Z_{\text{calc}} - Z)^2$ for different combinations (101) + (102) + (202) + (011) + (PQR), where $0 \leq P \leq 2$, $Q = 2$, and $1 \leq R \leq 3$. As seen in Fig. 5 we got low $U_i$-values for (021) and (122), corresponding to $\text{Cd}_2(\text{H}_2\text{Asc})_2 \text{HAsc}^+$ and $\text{Cd}_2(\text{H}_2\text{Asc})_2 \text{HAsc}^3+$. $C$ varied between 0.4 and 1.0 M, and $c = [\text{H}_2\text{Asc}]$ between 0.3 and 0.6 M. To get a broader range of $C$ we used data from part IV and picked out 134 points with $C$ in the interval $0.002 \leq C \leq 1.0$ M. Now (021) and (122) were tested minimizing $U_i$ using log $\beta_{101} = 4.36$, log $\beta_{102} = 4.45$, and log $\beta_{202} = 8.56$ from part I. We obtained:

$$\log (\beta_{011} \pm 3 \sigma) = 0.39 \pm 0.04$$
$$\log (\beta_{021} \pm 3 \sigma) = -0.81 \pm 0.05$$
$$\sigma(Z) = 0.0084$$

or

$$\log (\beta_{011} \pm 3 \sigma) = 0.42 \pm 0.02$$
$$\log (\beta_{122} \pm 3 \sigma) = 4.66 \pm 0.06$$
$$\sigma(Z) = 0.0055$$

Thus $\text{CdHAsc}^+$ and $\text{Cd}_2\text{H}_2\text{Asc}^3+$ ($R = 2$) give the "best" fit with the data. The final model is:

$$(101) + (102) + (202) + (011) + (122)$$

(12 e)

Refinement by least squares treatment (LETAGROP)

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

Final $H = H$ (calculated from analysis, cf. part II) + $\delta H$ (13)
Final $E_0 = E_0$ (calculated from a few acid points, cf. part II) + $\delta E_0$

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

The error, $\delta H = -4.9$ mM for $B = 1.4$ M and $C = 1.0$ M, seems high but not unreasonably so (= 1.6 % in $H$). We obtained the liquid junction potential $\equiv (-17.5 \pm 1)h$. $E_j$ seems independent of $B$ and $C$ in the present ionic media.

RESULT AND DISCUSSION

As the final result we propose the following reactions and constants valid in 3 M (Na, Cd)ClO$_4$ media at 25°C:

<table>
<thead>
<tr>
<th>pqr</th>
<th>Reaction</th>
<th>(log $\beta_{pqr} \pm 3\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>101</td>
<td>$\text{HAsc}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{Asc}$</td>
</tr>
<tr>
<td>2</td>
<td>102</td>
<td>$2\text{HAsc}^- + \text{H}^+ \rightleftharpoons \text{H}_3\text{Asc}^-$</td>
</tr>
<tr>
<td>3</td>
<td>202</td>
<td>$2\text{HAsc}^- + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{Asc}_2$</td>
</tr>
<tr>
<td>4</td>
<td>011</td>
<td>$\text{Cd}^{2+} + \text{HAsc}^- \rightleftharpoons \text{CdHAsc}^+$</td>
</tr>
<tr>
<td>5</td>
<td>122</td>
<td>$2\text{Cd}^{2+} + 2\text{HAsc}^- + \text{H}^+ \rightleftharpoons \text{Cd}_2\text{H}_2\text{Asc}_2^{3+}$</td>
</tr>
</tbody>
</table>

The solutions contain the pure ascorbic acid species H$_2$Asc, HAAsc$^-$, H$_3$Asc$_2$ and H$_2$Asc$_2$. The predominating cadmium species is CdHAsc$^+$. Probably Cd$_2$HAsc$_2$ is also present in the solution. The final model agrees very well with our result in parts I, III, and IV in this series.

Fig. 6. The distribution of ascorbic acid on different species as a function of log $h$. $B = 1.2$ M, $C = 1.0$ M. HALTAFAIL$^a$ was used for the calculations, taking the constants from Table 3. At a given value of log $h$ the fraction of ascorbic acid present as H$_2$B$_2$C is represented by the segment of a vertical line falling within the corresponding area.

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

Acknowledgements. We want to thank Professors Peder Kierkegaard, Arne Magnéli and Lars Gunnar Sillén for valuable help throughout this work.

We have learnt about the “Self medium technique” from especially Sirkka Hietanen and Lars Gunnar Sillén (Ref. 10) and from Georg Biedermann and Liberato Ciavatta (Ref. 6). Professor Sillén was kind enough to read and comment on the manuscript. Thanks are due to Dr. Sven Westman for revising the English text of this article.

We are obliged to the Royal Swedish Academy of Science for a grant to O. W. from the Hierta-Resius’ Fund.

A stipend from the University of Stockholm to O. W. is gratefully acknowledged.

We have gratefully received financial aid from Anskapesposten Främjande av ograduerade forskare vetenskapliga verksamhet, University of Stockholm.

This investigation was financially supported by the Tricentennial Fund of the Bank of Sweden, and by the Swedish Natural Science Research Council.

Computer calculations have been performed, using CDC 3600 at Uppsala Data-central (the programs LETAGROP, MESAK and HALTAFAIL), and IBM 1800 at Frescati, Stockholm (TRAVE).

REFERENCES


Received July 17, 1970.