Equilibrium Studies of \( \text{L-Ascorbate Ions} \)

II. Metal—Ascorbate Complexes Formed in Aqueous Solution, an Introduction

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Investigations of complexes between bivalent metal ions and ascorbic acid, \( \text{H}_2\text{Asc} \), have been started on the system \( \text{Cd(II)} - \text{HAsc}^- - \text{H}^+ \). The next two systems to be studied are \( \text{Ca(II)} - \text{HAsc}^- - \text{H}^+ \) and \( \text{Fe(II)} - \text{HAsc}^- - \text{H}^+ \). Some information necessary for these studies will be given in this article.

The formation of a complex \( \text{H}_2\text{Asc}_n \) can be written

\[
p\text{H}(h) + q\text{B}(b) + r\text{C}(c) \rightleftharpoons \text{H}_2\text{B}_q\text{C}_r(c_{\text{pqr}}) \quad c_{\text{pqr}} = \beta_{\text{pqr}}b^p c^r\tag{1}
\]

A complex \( \text{H}_2\text{B}_2\text{C} \) will be referred to as \( \text{PQR} \). Our aim is to determine \( p, q, r, \) and \( \beta_{\text{pqr}} \) for the predominant complexes, using data from emf titrations. We usually know the total concentrations of \( \text{H} \equiv \text{H}^+ \), \( \text{B} \equiv \text{Me}^{2+} \) and \( \text{C} \equiv \text{HAsc}^- \) from analysis and the free concentration of \( \text{H}^+ \) from emf measurements. These data are first treated by graphical methods to give information about the principal species in the solutions. The final equilibrium model is selected and refined by using the generalized least squares method LETAGROP.

The system \( \text{HAsc}^- - \text{H}^+ \). In part I of this work we have found that ascorbic acid is a dibasic acid with \( pK_{a1} = 4.36 \) and \( pK_{a2} = 11.34 \) in 3 M NaClO\(_4\) medium at 25°C. At high concentrations of ascorbic acid (\( \geq 0.25 \) M) we got evidence for the dimeric species \( \text{H}_2\text{Asc}_n \) and \( \text{H}_3\text{Asc}_n^- \).

The systems \( \text{Me}^{2+} - \text{H}^+ \). The hydrolysis of metal ions has been studied extensively in Sillén’s laboratories in Stockholm,\(^2\) \( \text{Cd}^{2+}, \text{Ca}^{2+} \) and \( \text{Fe}^{3+} \) can act as weak acids according to \( \text{Me}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{MeOH}^+ \). The dissociation constants are \( pK(\text{Cd}^{2+}) = 10.2,^3 pK(\text{Ca}^{2+}) = 13.6,^4 \) and \( pK(\text{Fe}^{3+}) = 9.5.\(^5 \) In the system \( \text{Cd(II)} - \text{H}^+ \), polynuclear species \( \text{Cd}_2\text{OH}^3^+ \) and \( \text{Cd}_4\text{OH}_4^4^+ \) are important (see Biedermann and Ciavatta, Ref. 3).

The systems \( \text{Me}^{4+} - \text{HAsc}^- - \text{H}^+ \). A summary of the species and the equilibrium constants for metal ascorbate equilibria in aqueous solutions found in the literature is given Table 1.
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<td>Stolyarov and</td>
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<td>$10^{-4} \leq [\text{Mo}^{4+}]_{\text{tot}} \leq 10^{-2} \text{M}$</td>
<td>MoHAasc</td>
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<td>Amantova</td>
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<td>$0.2 \leq [\text{H}<em>2\text{Asc}]</em>{\text{tot}} \leq 1 \text{ M}$</td>
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<td></td>
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<td>$2 \leq \text{pH} \leq 4$</td>
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<td>Singh et al.</td>
<td>Spectrophotometry</td>
<td>$10^{-8} \leq [\text{UO}<em>2^{4+}]</em>{\text{tot}} \leq 10^{-3} \text{M}$</td>
<td>UO$_4$HAasc$^+$</td>
<td>2.35</td>
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<td></td>
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<td>$0.01 \leq [\text{H}<em>2\text{Asc}]</em>{\text{tot}} \leq 1 \text{ M}$</td>
<td>UO$_4$(HAasc)$_2$</td>
<td>0.97</td>
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<td>$2 \leq \text{pH} \leq 5.8$</td>
<td>UO$_4$HAasc(OH)$_3$</td>
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<td></td>
<td>UO$_4$(HAasc)$_4$OH$^-$</td>
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<td>Sommer</td>
<td>Spectrophotometry</td>
<td>[H$<em>2$Asc]$</em>{\text{tot}}$ $&gt;$ 500[Ti(IV)]$_{\text{tot}}$</td>
<td>TiHAasc$^+$</td>
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<td>$\text{pH} \leq 4.5$</td>
<td>TiOHAsc$^+$</td>
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<td>TiO(HAasc)$_2$</td>
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<td>TiO(Aasc)$_4$</td>
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<td>TiO(Aasc)$_6$</td>
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<td>Sušić</td>
<td>Spectrophotometry</td>
<td>$\mu \rightarrow 0$</td>
<td>TiOHAsc$^+$</td>
<td>1.8</td>
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<td></td>
<td></td>
<td>$0.002 \leq [\text{H}<em>2\text{Asc}]</em>{\text{tot}} \leq 0.5 \text{ M}$</td>
<td>One anionic species</td>
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<td>$1.5 \leq \text{pH} \leq 8$</td>
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<tr>
<td>Veselinović et al.</td>
<td>Spectrophotometry, polarimetry, chromatography</td>
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<td>WO$_4$(Aasc)$_4$$^{2+}$</td>
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<tr>
<td>Novoselov et al.</td>
<td>Potentiometry (silver electrode)</td>
<td>$25^\circ \text{C}$ $2 \times 10^{-4} &lt; [\text{Ag}^+]_{\text{tot}} &lt; 4 \times 10^{-3} \text{M}$</td>
<td>AgH$_2$Asc$^+$</td>
<td>3.64 $\pm$ 0.05</td>
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<td></td>
<td></td>
<td>$3 \times 10^{-4} &lt; [\text{H}<em>2\text{Asc}]</em>{\text{tot}} &lt; 4 \times 10^{-5} \text{M}$</td>
<td></td>
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<tr>
<td>Sobkowska and</td>
<td>Potentiometry</td>
<td>20$^\circ \text{C}$; 1 M NaClO$_4$</td>
<td>UO$_4$HAasc$^+$</td>
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<td>Minczewski</td>
<td></td>
<td>$[\text{UO}<em>2^{4+}]</em>{\text{tot}} = 0.011 \text{ M}$</td>
<td>UO$_4$(HAasc)$_2$</td>
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<td>$\text{pH} = 3.45$</td>
<td>UO$_4$(HAasc)$_4$</td>
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<tr>
<td>Martell et al.</td>
<td>Potentiometry</td>
<td>$25^\circ \text{C}; \mu = 0.10$ (KNO$_3$)</td>
<td>UO$_4$HAasc$^+$</td>
<td>3.5 $\pm$ 0.1</td>
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<td></td>
<td>$0.4^\circ \text{C} \mu = 0.10$ (KNO$_3$)</td>
<td>CuHAasc$^+$</td>
<td>1.87</td>
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<tr>
<td>Veselinović and</td>
<td>Potentiometry</td>
<td>$25^\circ \text{C}, \mu \rightarrow 0$</td>
<td>MoHAasc$^+$</td>
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<tr>
<td>Sušić</td>
<td></td>
<td>$0.004 \leq [\text{Mo}^{4+}] \leq 0.6 \text{ M}$</td>
<td>(Mo, log $\beta$) = Mn, 1.1; Co, 1.4; Ni, 1.05; Zn, 1.0; Ca, 1.05; Cd, 1.3; Pb, 1.8;</td>
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<td></td>
<td></td>
<td>$0.005 \leq [\text{H}<em>2\text{Asc}]</em>{\text{tot}} \leq 0.6 \text{ M}$</td>
<td>UO$_4$HAasc$^+$</td>
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<td></td>
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<td>$2 \leq \text{pH} \leq 7$</td>
<td>UO$_4$HAascOH$^-$</td>
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<td>MeHAascOH</td>
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<td>MeHAasc(OH)$_3$</td>
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<td>AIHAasc$^+$</td>
<td>1.89 $\pm$ 0.1</td>
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<td>Al(Aasc)$_2$</td>
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<td></td>
<td></td>
<td>Al(Aasc)$_4$OH</td>
<td>3.55 $\pm$ 0.3</td>
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<td></td>
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<td></td>
<td>Al(Aasc)$_4$(OH)$_2$</td>
<td></td>
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<tr>
<td>Lai and Wang</td>
<td>Polarography</td>
<td>$0.132 \leq [\text{H}<em>2\text{Asc}]</em>{\text{tot}} \leq 1.0 \text{ M}$</td>
<td>{Pb(II)}$_4$(HAasc)$_2$H$_2$</td>
<td>A mixture of more than one kind of chelate species</td>
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<td>$2.5 \leq \text{pH} \leq 5.8$</td>
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<tr>
<td>Schubert and</td>
<td>Ion exchange</td>
<td>$\mu = 0.16$</td>
<td>CaHAasc$^+$</td>
<td>0.19</td>
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<tr>
<td>Lindenbaum et al.</td>
<td></td>
<td>$\text{pH} = 7.2 - 7.3$</td>
<td>SrHAasc$^+$</td>
<td>0.35</td>
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</table>
Rather weak complexes of the type Me(HAsc), seem to exist in acid solutions (pH < 5) and at low concentrations. In neutral solutions, chelate complexes and hydrolysed species have been found. Those can generally be written $H_p^p Me_q (HAsc)_r$, where $p$ is mostly negative, indicating that $H^+$ is split off when the complexes form. This means that $OH^-$ or Asc$^{3-}$, or both, are bound in the complexes.

Solutions containing metal ions and ascorbic acid absorb light in the visible or UV region (see Ref. 6).

**LIST OF SYMBOLS**

Concentrations are given in mol/l, and emf values in mV. The sums $\sum c_{pqr}$, $\sum p_{pqr}$, $\sum q_{pqr}$, and $\sum r_{pqr}$ are taken over all combinations of $pqr$, excluding 100, 010, and 001, which correspond to $h$, $b$, and $c$. Further limitations may be given.

- $B$ total concentration of $B = Me^{t+}$
- $B_0$ $B$ in the starting solutions $S_0$
- $B_T$ $B$ in the buret solution $T$
- $B_{c_{pqr}} = b + \sum_{r=0} c_{pqr}$
- $b$ free concentration of $B$, $b = [Me^{t+}]$
- $C$ total concentration of $C$
- $C_0$ $C$ in the starting solutions $S_0$
- $C_T$ $C$ in the buret solution $T$
- $c_{pqr}$
  - $c_{pqr} = [H_p^p B_q C_r] = \beta_{pqr} h^p b^q c^r$. Note that $c_{100} = h$, $c_{010} = b$, and $c_{001} = c$
  - cf. definition of $\beta_{pqr}$ below
- $E$ the measured emf
- $E_0 = (RT \ln 10/F) \log h + E_j$
- $\delta E_0$ systematic error in $E_0 = (E_0)_{corr} = E_0 + \delta E_0$
- $E_j$ liquid junction potential $E_j = j h + K_w j_{alk} h^{-1}$
- $H$ excess (analytical) concentration of $H^+$ over $H_2O$, $HAsc^-$, and $Me^{t+}$
- $H_0$ $H$ in the starting solution $S_0$
- $H_T$ $H$ in the buret solution $T$
- $\delta H$ systematic error in $H$; $H_{corr} = H + \delta H$
- $\sigma_p (H)$ standard deviation of $H$ defined as $\sigma(y)$ in Ref. 35.
- $h$ the free concentration of $H^+$, $h = [H^+]$
- $j$ and $j_{alk}$ constants in $E_j = j h + K_w j_{alk} h^{-1}$
- $K_w$ ionic product of water
- $p$ number of $H$ in the complex $H_p B_q C_r$
- $q$ average number of $H$ bound per complex $= \sum p_{pqr} / \sum c_{pqr}$
- $q$ number of $B$ in the complex $H_p B_q C_r$
- $q$ average number of $B$ bound per complex $= \sum q_{pqr} / \sum c_{pqr}$
- $r$ number of $C$ in the complex $H_p B_q C_r$
- $r$ average number of $C$ bound per complex $= \sum r_{pqr} / \sum c_{pqr}$

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\[ S \] equilibrium solution
\[ S_0 \] S before addition of buret solution T
\[ T \] buret solution
\[ U_H \] \[ U_H = \sum (H_{calc} - H)^2 \] The sums are taken over all experimental points
\[ U_Z \] \[ U_Z = \sum (Z_{calc} - Z)^2 \] or part of them.
\[ V \] volume of buret solution T added to \( S_0 \)
\[ V_0 \] volume of \( S_0 \)
\[ Z_{H/C} = Z \] average number of H bound per C = \[ \sum \rho_{pqr} (c + \sum \rho_{pqr}) \]
\[ Z_{H/B} \] average number of H bound per B = \[ \sum \rho_{qqr} (b + \sum \rho_{pqr}) \]
\[ Z_{C/B} \] average number of C bound per B = \[ \sum \rho_{pqr} (b + \sum \rho_{pqr}) \]
\[ Z_{noc} \] average number of H bound per B in the species \( H_p B_q \) (that is in \( Me_r(OH)_s = \sum \rho_{pqr} (b + \sum \rho_{pqr}) \)
\[ \delta Z \] systematic error in Z
\[ \sigma(Z) \] standard deviation of Z defined as \( \sigma(y) \) in Ref. 35a.
\[ \alpha_{pqr} = \alpha_c \] the fraction of ascorbic acid present in \( H_p B_q C_r \)
\[ \beta_{pqr} \] equilibrium constant for the formation of \( H_p B_q C_r \). \[ \beta_{pqr} = c_{pqr} h^p b^q c^r \]
we define \( \beta_{100} = \beta_{010} = \beta_{001} = 1 \)

EXPERIMENTAL

Chemicals and analysis

\( HClO_4, NaOH, \) and L-ascorbic acid are prepared and analysed in the same way as in part I.\(^1\)

\( NaCl \). Merck’s p.a. was dried at 250°C and used without further purification.

\( NaClO_4 \) was first prepared as described in part I,\(^1\) but after some tests on the amount of protolytic impurities we found that one recrystallisation (instead of two) of \( NaHCO_3 \) was enough (see below).

\( H_2 O \). The water was purified by distillation of water from a central ion exchanger. The distilled water was passed through a column containing mixed cation-anion exchanger. The conductivity of water used in our experiments mostly had values within \( \kappa = (2 \pm 1) \times 10^{-4} \) ohm\(^{-1}\) cm\(^{-1}\), sometimes lower.

Purity of the medium, 3 M \( NaClO_4 \) in water. Typical experiments:

(1) A solution was tested for redox- and protolytic impurities as proposed by Cavatorta;\(^2\) 40 ml of a solution, containing 2 mM \( HClO_4 \) and 3 M \( NaClO_4 \) in a 250 ml parafinised flask of Jena glass, was titrated using a coulometer, measuring \( h = [H^+] \) by means of a glass electrode. \( HClO_4 \) was added once more and titrated. Gran diagrams \(^3\) were calculated (Fig. 1). The points from the two runs fall on the same line before the equivalence point; this indicates that no redox impurities are present in the solution tested.

In Fig. 1 one can read off the amount of protolytic impurity. The concentration of the “dirt acid” was found to be \( C_{HX} = (60 \pm 20) \) µM in a 3 M \( NaClO_4 \) solution.

(2) Another 40 ml solution containing 2 mM \( H_2 Asc \), 1 mM \( HClO_4 \) and 3 M \( NaClO_4 \) was titrated using the coulometer (Fig. 2). The concentration of the “dirt acid” \( C_{HX} \), its dissociation constant \( K_{HX} \), and the first dissociation constant of \( H_2 Asc \) were determined using \( \text{LETAGROP}: C_{HX} = (67 \pm 67) \mu M, K_{HX} = (4 \pm 4) \times 10^{-4} M^{-1} \) and \( -log K_a = 4.34 \pm 0.011 \). The errors are 3\( \sigma \), where \( \sigma \) is the standard deviation. The value of log \( K_a \) agrees well with that found in part I;\(^1\) 4.35 ± 0.006. The amount of protolytic impurity seems to be much smaller than the concentration of ascorbic acid in the solution. In fact, \( C_{HX} \) was too small to be ascertained, but it appears to be of the same order as the value obtained by Cavatorta’s method. At any rate, the “dirt acid” does not influence the determination.

**Fig. 1.** Gran plot for a titration of 1 mM of HClO₄ in 40.09 ml 3 M NaClO₄ solution. H⁺ was removed by electrolysis using a coulometer: 

\[ 
\text{H}^+ + e^- \rightarrow \frac{1}{2} \text{H}_2(g) ; \quad Y_0 = 40.09 \times 10^{5.89}; Y_\infty = 40.09 \times 10^{10.65} \times e^{-}\frac{nF}{\mu F} 
\]

\( n \) = the number of microfaradays generated by the coulometer. Points from the first run marked with ○ and points from the second run with ●. \( C_{HX} \frac{Y_0}{n} \) = the amount of protolytic impurity, \( C_{HX} = 60 \ \mu M \).

**Fig. 2.** \( Z(\log h) \) = the average number of H⁺ per ascorbic acid as a function of \( \log h \). The total concentration of ascorbic acid = 2 mM. The full line corresponds to \( \log h = 4.34 \). Experimental points marked by triangles.

of the dissociation constant for ascorbic acid. The level of impurities is sufficiently low for our purpose, choosing the total concentration of ascorbic acid always greater than, or equal to 2 mM. The identification of the “dirt acid” is difficult. It may be carbonic acid, silicic acid or an organic rest from the ion exchanger.

**Apparatus**

The saltbridge, potentiometer and thermostat are the same as used in part I.¹ The hydrogen electrodes and Ag, AgCl-electrodes are prepared as in part I. Glass electrodes with type numbers 41206 and 40495 from Beckman are used.

Coulometer. A coulometric analyzer from Leeds and Northrup Co. was used as a source of a constant current: 64.35 mA, 6.43 mA, or 0.6434 mA. The coulometer contains an equipment for time measurement (a synchronous motor) and the number of microfaraday delivered can be directly read off. The constant current was calibrated against standard resistors. The precision was 0.02 %.

The volumetric equipment, such as burets and pipets, were calibrated using water.

**EMF MEASUREMENTS AND TITRATION PROCEDURE**

Emf of the following cells is measured:* 

- glass electrode |S| RE +

- Pt, H₂ (1 atm) |S| RE +

As reference electrode we use:

\[ RE = 3 \text{ M NaClO}_4|2.990 \text{ M NaClO}_4, 0.010 \text{ M NaCl, saturated with AgCl}|AgCl,Ag \]

\[ \text{or } RE = 3 \text{ M NaClO}_4|2.990 \text{ M NaClO}_4, 0.010 \text{ M AgClO}_4|AgCl,Ag \]

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* We cannot use a quinhydrone electrode, since quinhydrone reacts with ascorbic acid.

Assuming the activity coefficients to be constant, the following expression for $E$ is valid $^{18, 19}$ (at 25°C):

$$E = E_0 - 59.155 \log h + E_j$$  \hspace{1cm} (2)

$$E_j = jh + K_{w_j}h^{-1}$$

In our solutions often $\log h > -11$, which allows us to write $E_j = jh$ (cf. Ref. 19). The clear solution $S$ contains $V$ ml from a buret solution $T$ added to $V_0$ ml of a starting solution $S_0$. To avoid strong alkaline solutions containing metal ions or ascorbic acid the $T$ solution is, in forward titrations, added from two burets as indicated in Table 2.

**Table 2. The composition of solutions $S$, $S_0$, $T$, $T_1$ and $T_2$.**

<table>
<thead>
<tr>
<th></th>
<th>$[\text{H}^+]_{\text{tot}}$</th>
<th>$[\text{Mo}^{3+}]_{\text{tot}}$</th>
<th>$[\text{H}<em>2\text{Asc}]</em>{\text{tot}}$</th>
<th>$[\text{ClO}_4^-]$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$</td>
<td>$H$</td>
<td>$B$</td>
<td>$C$</td>
<td>$3$</td>
<td>(Concentrations in mol/l)</td>
</tr>
<tr>
<td>$S_0$</td>
<td>$H_0$</td>
<td>$B_0$</td>
<td>$C_0$</td>
<td>$3$</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>$H_T &lt; 0$</td>
<td>$B_T$</td>
<td>$C_0$</td>
<td>$3$</td>
<td>Forward titration</td>
</tr>
<tr>
<td>$T_1$</td>
<td>$[\text{H}^+]_{\text{tot}} &lt; 0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>NaOH solution</td>
</tr>
<tr>
<td>$T_2$</td>
<td>$[\text{H}^+]_{\text{tot}} &gt; 0$</td>
<td>$2B_T$</td>
<td>$2C_0$</td>
<td>$6$</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>$H_T &gt; 0$</td>
<td>$B_T$</td>
<td>$C_0$</td>
<td>$3$</td>
<td>Back titration</td>
</tr>
</tbody>
</table>

Thus, in a titration, $B$ and $C$ are kept constant, while $H$ is varied:

$$H = (VH_T + V_0H_0)/(f_vV + V_0) ; \quad B_0 = B_T; \quad C_0 = C_T$$  \hspace{1cm} (3)

$f_v = 0$ for a coulometric titration

$f_v = 1$ for an ordinary buret titration

Measurements with a cadmium amalgam electrode $^{30}$ will be used to check results from $(H, h)_{B,C}$ data measured on the system Cd(II) - HAsc$^-$/H$^+$. For more details we refer to following articles of this series.

**EQUILIBRIUM AND MASS BALANCE EQUATIONS**

The law of mass action gives for the general reaction (1)

$$c_{pqr} = \beta_{pqr}h^p b^q c^r, \quad \text{where} \quad c_{pqr} = [H_pB_qC_r]$$  \hspace{1cm} (4)

The concentration of ascorbic acid not bound to metal is denoted by $C_{\text{asc}}$ and the amount of H$^+$ bound in these species not containing metal by $C_{\text{noB}}Z_{\text{noB}}$:

$$C_{\text{asc}} = [C] + \sum r[H_pC_r] = c + \sum q c_{pqr}$$  \hspace{1cm} (5 a)

$$C_{\text{noB}}Z_{\text{noB}} = \sum p[H_pC_r] = \sum q c_{pqr}$$  \hspace{1cm} (5 b)

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The concentration of metal not bound to ascorbic acid is denoted by $B_{noC}$, and the amount of $H^+$ bound in these species by $B_{noC}Z_{noC}$:

$$B_{noC} = [B] + \sum q[Me_q(OH)]_n = b + \sum qc_{pqr}$$  \hspace{1cm} (6a)

$$B_{noC}Z_{noC} = \sum n[Me_q(OH)]_n = \sum p_{pqr}$$  \hspace{1cm} (6b)

The total concentrations may now be written as follows:

$$H = h - K_v h^{-1} + \sum p_{pqr}$$  \hspace{1cm} (7a)

$$B = B_{noC} + \sum r_{q0} c_{pqr}$$  \hspace{1cm} (7b)

$$C = C_{noB} + \sum r_{q0} c_{pqr}$$  \hspace{1cm} (7c)

We shall define the quantities $Z_{H/C}$, $Z_{H/B}$, and $Z_{C/B}$:

$$C Z_{H/C} = H - h + K_v h^{-1}$$  \hspace{1cm} (8a)

$$B Z_{H/B} = H - h + K_v h^{-1}$$  \hspace{1cm} (8b)

$$B Z_{C/B} = C - C_{noB}$$  \hspace{1cm} (8c)

$Z = Z_{H/C}$ is the average number of $H^+$ bound per C

$Z_{H/B}$ is the average number of $H^+$ bound per B

$Z_{C/B}$ is the average number of C bound per B

Note that $(H - h + K_v h^{-1})$ is the concentration of $H^+$ bound (in mol/l), and that $(C - C_{noB})$ is the concentration of C bound in complexes with B.

NOTES ON THE CALCULATION AND USE OF Z-FUNCTIONS

For graphical representation of data and for least squares refinement we use $Z = Z_{H/C}$, which can easily be obtained from eqn. (8a), without approximations. In the graphical treatment we use $Z_{H/C}$, $Z_{H/B}$, and $Z_{C/B}$. To get more information about the complexes $H\cdot B\cdot C$, with $q \neq 0$ and $r \neq 0$ we subtract the contribution to $H$ from $H_p C_p$ and $H_p B_q$ in $Z_{H/C}$ and $Z_{H/B}$. From eqns. (8a), (8b), and (8c) we thus obtain:

$$Z'_{H/C} = Z_{H/C} - H'/C$$  \hspace{1cm} (9a)

$$Z'_{H/B} = Z_{H/B} - H'/B$$  \hspace{1cm} (9b)

where $H' = B_{noC}Z_{noC} + C_{noB}Z_{noB}$

$$Z_{C/B} = (C - C_{noB})/B$$  \hspace{1cm} (9c)

In the graphical treatment we often introduce approximations, and therefore we think that the result must not be regarded as final, but as a starting point for rigorous least squares treatment.

The quantities $B_{noC}$ and $Z_{noC}$. The amount of hydrolysed species $Me_q(OH)_n$ will mostly be very small in our solutions, that is $B_{noC}Z_{noC} \approx 0$. However, in solutions with high $B$ values, we must correct for $H^+$ bound in $Me_q(OH)_n$ species (at most a few per cent). In that case we introduce the approximations $b \approx B$ and $B_{noC} \approx B$.  

$Z_{\text{noc}}$ can be obtained from eqns. (6 a–b), approximating $b \approx B$. Thus, if the equilibrium constants, $\beta_{Pq}$ are known:

$$Z_{\text{noc}} = \sum p \beta_{Pq} h^q B^q (b + \sum q \beta_{Pq} h^q B^q)$$  \hspace{1cm} (10)

The quantities $C_{\text{noB}}$ and $Z_{\text{noB}}$. $C_{\text{noB}}$ can be obtained in different ways:

(I a) In acid solutions, say $-4.5 \leq \log h \leq 2.0$, B,C, complexes are those principally formed. If B,$C_\text{p}$, are the only metal complexes, and C=HAsc$^-$ is taken as the zero point for H, then $Z'_{\text{H/C}} = 0$. Now, if we know $Z_{\text{H/C}}$, $B_{\text{noc}}Z_{\text{noc}}$, and $Z_{\text{pH}}$ (see eqn. 12 below), we can calculate $C_{\text{noB}}$ from eqn. (9 a).

(I b) In neutral or alkaline solutions, say $-12 \leq \log h \leq -7$, it could be reasonable to assume that, principally, B$_4$(H$_3$C)$_4$, complexes are formed. In this case, one may choose Asc$^2-$ as the zero point for H, rewriting the complexes as B,$C_\text{p}$, choosing C=Asc$^2$. Now again $Z'_{\text{H/C}} = 0$, and $C_{\text{noB}}$ can be calculated from eqn. (9 a); cf. (I a).

(2) In the range $-10 \leq \log h \leq -5$, HAsc$^-$ is the predominating ascorbic acid species. Choosing HAsc$^-$ as zero point for H, the small amount of H$^+$ bound in H$_2$Asc and Asc$^{2-}$ can be approximated to $Z_{\text{noB}}$. Thus $C_{\text{noB}} \approx C$ (cf. eqn. (5b)). This approximation is useful, e.g. when calculating $Z'_{\text{H/B}}$ from eqn. (9 b).

(3) Having a series of measurements with different $C$ values and the same $B$ value, one can use a formula derived by Österberg$^{20,22}$ to calculate $C_{\text{noB}}$:

$$\log (C_{\text{noB}}/C) = -\log C_{\text{noB}} [C_{\text{noB}}]_h = h_0 + \int_{\log h_0}^{\log h} [Z_{\text{noB}} - Z - (\partial Z/\partial \ln C)_{h,B}] d \log h$$ \hspace{1cm} (11)

($B, C$ constant)

This equation was derived starting from the general approach outlined by Sillén,$^{21}$ and it requires accurate data and the validity of the law of mass action. One must also know $C_{\text{noB}}$ of one point $h = h_0$.

$Z_{\text{noB}}$ can be calculated from the eqns. (5 a) and (5 b). Regarding only the species HC, C, and H$_3$C we get:

$$Z_{\text{noB}} = (\beta_{100} h - \beta_{101} h^{-1})/(1 + \beta_{100} h + \beta_{101} h^{-1})$$ \hspace{1cm} (12)

$\beta_{101}$ and $\beta_{101}$ are known from part I$^1$.

**EQUILIBRIUM ANALYSIS**

*Data collection* is carried out as potentiometric titrations at 25°C. Usually we keep $B$ and $C$ constant in the equilibrium solution S. $H$ is varied by additions from a buret, cf. eqn. (3). Suitable electrodes are used to measure $h$, cf. eqn. (2). To obtain data $(H, h)_{B,C}$ over a large concentration range of $B$ and $C$, both the “inert medium method”$^{20,18,22-25}$ and the “self medium method”$^{26,3,27,28}$ are used. NaClO$_4$ is added, so that in all solutions [ClO$_4^-$] = 3 M, to keep the activity coefficients constant.

*Data treatment* is carried out in essentially four steps.

1. *Reduction of primary data* $(V, E)_{B,C}$. From a few points in the range $0.01 \leq h \leq 0.15$ M of each titration we use Gran extrapolation$^{29}$ to correct for small analytical errors in $H_0$ or $H_T$. The same points are used to calculate

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$E\textsubscript{f}$ from eqn. (2) assuming $H^+$, Me$^{3+}$, H$_2$Asc, and a small amount of HAsc$^-$ to be present.\textsuperscript{41} We can use $E\textsubscript{f} = 17$ if the equilibrium solution S contains 3 M NaClO$_4$ and log $h > -11.\textsuperscript{1,13,18,23,31}$ In other cases, $E\textsubscript{f}$ will be checked.\textsuperscript{19,41} $(V, E)_{B,C}$ is then transformed to some functions, e.g. $(H, h)_{B,C}$, eqns. (2) and (3), and various $Z$-functions, eqns. (8 a) and (9 a-c). A computer program, TRAVE,\textsuperscript{41} makes these calculations comfortable.

2. Graphical treatment is used to limit the number of triplets $(p, q, r)$, from which the final combination giving the "best" fit with the data is selected. General methods frequently used for two component systems,\textsuperscript{22-25} containing complexes $A\textsubscript{p}B\textsubscript{q}C\textsubscript{r}$, will be applied, especially curve fitting, using normalized functions proposed by Sillen in Ref. 32 (see also Rossotti-Rossotti's textbook).\textsuperscript{33} The MESA$\bar{a}$K method\textsuperscript{21,19,33} can give valuable information about the average composition of the complexes, i.e. $\bar{p}$, $\bar{q}$, $\bar{r}$. For applications to three component systems with complexes $A\textsubscript{p}B\textsubscript{q}C\textsubscript{r}$, see Österberg\textsuperscript{22} and Ciavatta et al.\textsuperscript{34} In the graphical treatment we plot various functions. When calculating these functions, approximations may be introduced. In the subsequent LETAGROP\textsuperscript{35-39} calculations, however, we use the primary data $(V, E)_{B,C}$ directly without those approximations. The graphical treatment can thus give information about the principle species in the solutions.

3. Selection of a final combination of complexes giving the "best" fit with the data. We use for this purpose the generalized least squares program LETAGROP\textsuperscript{38,39} minimizing $U = \sum (Z\textsubscript{calc} - Z)^2$. Sometimes, however, we minimize $U = \sum (H\textsubscript{calc} - H)^2$ giving higher weight to large $C$ values. The sums are taken over all experimental points or a part of them. We start by testing various combinations of complexes indicated by the graphical treatment. When a set of complexes, fitting the data well, is found, we systematically try new complexes using the "SPECIES SELECTOR" in LETAGROP.\textsuperscript{37}

4. Refinement of the final equilibrium model, using LETAGROP. We minimize $U = \sum \omega (Z\textsubscript{calc} - Z)^2$. For our data, $(Z\textsubscript{calc} - Z)$ is of the same order of magnitude, viz. $\sim 0.01$ for all $H$, $B$, $C$ values used. We therefore choose the weigh factor $\omega = 1$. The systematic errors are treated as parameters.\textsuperscript{39} We assume small errors $\delta H$ in $H$, and $\delta E\textsubscript{f}$ in $E\textsubscript{f}$. We also test for a protolytic impurity of concentration $C\textsubscript{HX}$ and with the dissociation constant $K\textsubscript{HX}$.

The result is presented as equilibrium reactions with their equilibrium constants. In the following papers of this series we present tables giving for each experimental point $V$, $E$, log $h$, $H$, $(H\textsubscript{calc} - H)$.

In diagrams, $Z$ (log $h$)$_{B,C}$ and $Z\textsubscript{calc}$ (log $h$)$_{B,C}$ are shown. $Z\textsubscript{calc}$ and the distribution curves $a\rho r$, can be calculated by HALTAFALL.\textsuperscript{40}

NOTES ON THE USE OF THE SELF MEDIUM METHOD

When collecting data $(H, h)_{B,C}$ we can choose $h$ high and constant values of $B$ and $C$, e.g. 0.4 or 1.4 M, keeping $[ClO_4^-] = 3$ M, and allowing for only small changes in $H$. This is advantageous for two reasons: (1) We get data at high $B$, $C$ levels without changing the medium very much. The activity coefficients are then approximately constant for each titration. (2) If we keep $B$ or $C$ high and constant, the mathematical treatment of data is simplified. We can approximate $b \approx B$, and $c \approx C$. The complexes $H\rho B\textsubscript{C}$, can be treated

formally as $H_2C_r$ (with $B$ in the medium), as $H_B$ (with $C$ in the medium)
or as $H_p$ (with both $B$ and $C$ in the medium); cf. Ref. 26.

For example, with $B$ in the medium, we change $H$ so little that always $b \approx B$, keeping $C \ll B$. A series of titrations at different $C$-levels and one constant $B$-level give $p$, $r$, and $\beta_{pr}^+$ for $H_2C_r$, formally written for $H_B$ and $C_r$, since $q$ cannot be determined, while $B$ is constant:

$$[H_B] = [H_p B] = \beta_{pr} \ln \frac{B}{C} = \beta_{pr}^{-1} h B,$$

thus $\beta_{pr}^+ = \beta_{pr}^+ B^\alpha$.

The values of $q$ can be determined by analysis of $\beta_{pr}^+(B) = \beta_{pr} B^q$, using data from media with different values of $B$.

We assume, when comparing different media, that the activity coefficient quotient $f$ in the exact expression for the equilibrium constant $\beta_{pr}$ only varies to a negligible extent from one medium to another. Thus, we assume that $f_s = f_p B^{-1}$, a constant in $\beta_{sr} = \frac{f_s h}{f_p B^{-1} c}$. The activity scale is so defined that $f$ approaches unity when the solution approaches pure medium.

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