ON COMPLEX CALCIUM CITRATE

BY

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The hypothesis that calcium ions form a complex with citrate ions was first put forward by SABBATANI (1) and has since then been generally accepted. The hypothesis has found support in works on the conductivity of solutions of calcium salts and citrates by SHEAR and KRAMER (2), SHEAR, KRAMER and RESNIKOFF (3), WILEY (4), and MULLI and STANDENATH (5), in studies on the solubility of calcium carbonate in solutions of sodium citrate by HASTINGS, MURRAY, and SENDROY (6), and biological experiments by CLARK, PERCIVAL and STEWART (7), STEWART and PERCIVAL (8), SHELLING, and MARSLOW (9) and others, but the first quantitative determination of the ionization constant of calcium citrate was made by HASTINGS, McLEAN, EICHELBERGER, HALL and DA COSTA (10).

The findings of these authors are in agreement with the following scheme of reaction

$$Ca^{++} + Cit^{---} = CaCit^- \qquad (1)$$

and the dissociation constant of the complex

$$\frac{C_{Ca^{++}} C_{Cit^{---}}}{C_{CaCit^-}} = K_{CaCit^-} \qquad (2)$$

was found to be $K = 6.0 \cdot 10^{-4}$ at 22°—23°C. ionic strength $\mu = 0.155 - 0.163$ and pH = 7.4.

The amount of ionized calcium was determined by means of the amplitude of contraction of an isolated frog heart, a method described by MCLEAN and HASTINGS (11).

Though this work leaves no doubt as to the correctness of the above assumption, it was thought desirable to extend the investigation to a greater range of pH and μ. This could not be done by the frog heart method, and another method was adopted.

Theoretical.

In the present investigation the concentration of calcium ions was determined by the solubility of calcium iodate. The solubility of calcium iodate $Ca(IO_3)_2 6H_2O$ has been determined by KILDE (12) who found the activity solubility constant L_0 as given by relation

$$\begin{aligned} L_0 = A_{Ca++} \cdot A_{IO_3^-}^2 = C_{Ca++} \cdot f_{Ca++} \cdot C_{IO_3^-}^2 \cdot f_{IO_3^-}^2 = \\ = L \cdot f_{Ca++} \cdot f_{IO_3^-}^2 = L \cdot f_{Ca(IO_3)_2}^3 \end{aligned} \Bigg\} \quad (3)$$

$\Big(A_{Ca++}$ and $A_{IO_3^-}$ are the activities of calcium ions and iodate ions respectively, f_{Ca++} and $f_{IO_3^-}$ are the activity coefficients of calcium ions and iodate ions. $L = C_{Ca++} \cdot C_{IO_3^-}^2$ is the concentration solubility constant and $f_{Ca(IO_3)_2} = \sqrt[3]{f_{Ca++} \cdot f_{IO_3^-}^2}$ is the mean activity coefficient of the ions of calcium iodate.$\Big)$

at 25°C. to be $L_0 = 0.736 \ 10^{-6}$.

KILDE also found that the relation between the mean activity coefficient and the ionic strength μ could be expressed as follows:

$$pf_{Ca(IO_3)_2} = 1.008 \sqrt{\mu} - 0.78 \mu \quad \text{at } 25°C. \quad (4)$$

This formula is valid up to $\mu = 0.2$, i. e. if the ionic strength of a solution is known and lies within the limits $0 < \mu < 0.2$

the mean activity coefficient and hence the concentration solubility constant can be calculated.

The calcium ion concentration of a solution saturated with calcium iodate is given by

$$C_{Ca^{++}} = \frac{L}{C_{IO_3^-}^2} \qquad (5)$$

or under the assumption that all iodate present as ionized

$$C_{Ca^{++}} = \frac{L}{(C_{total\ iodate})^2}. \qquad (6)$$

If a solution contains a constituent, say citrate, that combines with calcium ions forming a complex, the concentration of this complex can be calculated by difference

$$C_{CaCit^-} = C_{total\ Ca} - C_{Ca^{++}} \qquad (7)$$

and the citrate ion concentration is

$$C_{Cit^{---}} = C_{total\ Cit} - C_{CaCit^-} \qquad (8)$$

assuming that calcium and citrate reacts according to scheme (1) and that the pH of the solution is such that the citric acid is completely ionized.

In pure water the solubility of calcium iodate is 0.00784 m at 25°C., and the solubility increases with increasing ionic strength. Since calcium citrate is only fairly soluble and it is desirable to have the molar concentration of calcium and citrate of the same order of magnitude, the concentration of calcium attained by simply saturating a solution of sodium citrate with calcium iodate is too great. To secure a concentration of calcium of the desired magnitude, potassium iodate was added to the solutions in order to reduce the solubility of calcium iodate. The solutions furthermore held a certain amount of sodium chloride to reduce the medium effect of varying concentrations of calcium and citrate.

Experimental.

The solutions were made up from standard solutions of sodium chloride (Merck. Zur Analyse dried) potassium iodate (Merck. Zur Analyse) and sodium citrate (Citric acid nach Sörensen + sodium hydroxide).

Calcium iodate was precipitated from a solution of potassium iodate with calcium chloride. The precipitate was very thoroughly washed with water and dried at room temperature and each new sample was checked.

The solutions were saturated with calcium iodate by shaking over night in a thermostat at 25°C., and samples were withdrawn for analysis of calcium (Kramer and Tisdall (13)) and iodate (addition of potassium iodide and hydrochloric acid and titration with sodium thiosulfate).

As already pointed out potassium iodate was added to lessen the solubility of calcium iodate. In some experiments the concentration of calcium was only $^1/_{10}$—$^1/_{20}$ of that of iodate. Since in the work of Kilde (12), these extreme

Table I.

Solubility Product of Calcium Iodate.

NaCl	KIO_3	IO_3 found	Ca found	μ	$L\,10^6$	$L_{cal}\,10^6$
M	M	M	M			
0.0450	0.0450	0.0482	0.00163	0.0949	3.80	3.76
0.0400	0.0500	0.0527	0.00138	0.0941	3.82	3.74
0.0650	0.0450	0.0486	0.00176	0.1153	4.16	4.20
0.0550	0.0550	0.0578	0.00130	0.1140	4.35	4.17
0.0850	0.0450	0.0489	0.00190	0.1357	4.55	4.61
0.0800	0.0500	0.0530	0.00161	0.1347	4.53	4.59
0.0750	0.0550	0.0574	0.00138	0.1339	4.56	4.58
0.0700	0.0600	0.0621	0.00120	0.1334	4.63	4.57
0.1150	0.0450	0.0496	0.00209	0.1665	5.14	5.16
0.1100	0.0500	0.0536	0.00181	0.1654	5.20	5.15
0.1050	0.0550	0.0578	0.00153	0.1645	5.12	5.13
0.1000	0.0600	0.0624	0.00127	0.1637	4.93	5.12

concentrations of calcium and iodate have not been used, we found it desirable to ascertain whether the solubility product was not influenced hereby. In table I, L is the solubility product found by us. L_{cal} is the solubility product computed by means of (3) and (4) putting $L_0 = 0.736 \ 10^{-6}$. It will be seen that there is perfect agreement, and that potassium iodate has no specific effect. By later experiments it has proved somewhat difficult to attain a constant preparation of calcium iodate, the solubitity products for some preparations being about 2—6 per cent above those calculated. This seems to be due to minor impurities.

Continued experiments are being made in order to solve this problem.

The solubility of calcium iodate was then determined in solutions containing sodium citrate. The solubility was much greater than the solubility of calcium iodate in mixtures of sodium chloride of the same ionic strength. In table II Ca_{obs} is the total calcium concentration found, Ca_{cal} is the calcium ion concentration calculated by means of (3),

Table II.

Observed and Calculated Concentration of Calcium in Solutions Containing Sodium Citrate.

Na₃Cit 0.005 m.   Ionic Strength 0.1341 – 0.1396.

Ca_{obs} M	0.00639	0.00576	0.00550	0.00516	0.00492	0.00465
Ca_{cal} M	0.00258	0.00211	0.00179	0.00148	0.00129	0.00112

Table III.

Observed and Calculated Concentration of Calcium in Solutions Containing Potassium Cobolticyanide.

K₃Co(CN)₆ 0.005 m.   Ionic Strength 0.1247—0.1308.

Ca_{obs} M	0.00347	0.00293	0.00208	0.00171	0.00147
Ca_{cal} M	0.00344	0.00294	0.00210	0.00177	0.00151

Table IV.

Dissociation Constant of Calcium Citrate.

a. $NaCl + KIO_3 = 0.07$ m, Na_3Cit 0.005 m, $\mu = 0.0917—0.0926$.

observed		calculated				
IO_3 M	Ca M	Ca^{++} M	$CaCit^-$ M	Cit^{---} M	$K_{CaCit^-} \cdot 10^4$	pK_{CaCit^-}
0.0556	0.00513	0.00120	0.00393	0.00107	3.27	3.48
0.0599	0.00482	0.00103	0.00379	0.00121	3.28	3.48
0.0643	0.00455	0.00089	0.00366	0.00134	3.29	3.48
0.0695	0.00423	0.00077	0.00346	0.00154	3.43	3.46
0.0686	0.00438	0.00078	0.00360	0.00140	3.08	3.51
				Mean value...	3.27	3.48

b. $NaCl + KIO_3 = 0.09$ m, Na_3Cit 0.005 m, $\mu = 0.1122—0.1150$.

observed		calculated				
IO_3 M	Ca M	Ca^{++} M	$CaCit^-$ M	Cit^{---} M	$K_{CaCit^-} \cdot 10^4$	pK_{CaCit^-}
0.0433	0.00639	0.00224	0.00415	0.00085	4.59	3.34
0.0431	0.00635	0.00225	0.00410	0.00090	4.94	3.31
0.0476	0.00576	0.00185	0.00391	0.00109	5.15	3.29
0.0478	0.00589	0.00182	0.00407	0.00093	4.16	3.38
0.0512	0.00550	0.00156	0.00394	0.00106	4.20	3.38
0.0558	0.00516	0.00133	0.00383	0.00117	4.06	3.39
0.0554	0.00520	0.00135	0.90385	0.00115	4.04	3.39
0.0599	0.00492	0.00115	0.00377	0.00123	3.76	3.42
0.0598	0.00481	0.00116	0.00365	0.00135	4.29	3.37
0.0643	0.00465	0.00100	0.00365	0.00135	3.70	3.43
0.0642	0.00455	0.00100	0.00355	0.00145	4.08	3.39
0.0643	0.00452	0.00100	0.00352	0.00148	4.21	3.38
				Mean value...	4.26	3.37

c. $NaCl + KIO_3 = 0.110$ m. Na_3Cit 0.005 m, $\mu = 0.1323—0.1333$.

observed		calculated				
IO_3 M	Ca M	Ca^{++} M	$CaCit^-$ M	Cit^{---} M	$K_{CaCit^-} \cdot 10^4$	pK_{CaCit^-}
0.0560	0.00529	0.00145	0.00384	0.00116	4.40	3.36
0.0598	0.00497	0.00127	0.00370	0.00130	4.46	3.35
0.0644	0.00468	0.00110	0.00358	0.00142	4.36	3.36
0.0692	0.00436	0.00095	0.00341	0.00159	˙4.44	3.35
0.0682	0.00437	0.00097	0.00340	0.00160	4.58	3.34
				Mean value...	4.45	3.35

Table IV.
(Continued).

d. $NaCl + KIO_3 = 0.125$ m, Na_3 Cit 0.005 m, $\mu = 0.1480—0.1491$.

observed		calculated				
IO_3 M	Ca M	Ca^{++} M	$CaCit^-$ M	Cit^{---} M	$K_{CaCit-}10^4$	pK_{CaCit-}
0.0558	0.00520	0.00156	0.00364	0.00136	5.83	3.23
0.0556	0.00547	9.00156	0.00391	0.00109	4.35	3.36
0.0598	0.00500	0.00135	0.00365	0.00135	5.00	3.30
0.0593	0.00494	0.00138	0.00356	0.00144	5.59	3.25
0.0642	0.00460	0.00117	0.00343	0.00157	5.36	3.27
0.0637	0.00456	0.00120	0.00336	0.00164	5.86	3.23
0.0690	0.00443	0.00102	0.00341	0.00159	4.76	3.32
0.0682	0.00432	0.00104	0.00328	0.00172	5.46	3.26
				Mean value...	5.25	3.28

e. $NaCl + KIO_3 = 0.140$ m, Na_3 Cit 0.005 m, $\mu = 0.1637—0.1654$.

observed		calculated				
IO_3 M	Ca M	Ca^{++} M	$CaCit^-$ M	Cit^{---} M	$K_{CaCit-}10^4$	pK_{CaCit-}
0.0568	0.00508	0.00160	0.00348	0.00152	6.99	3.16
0.0558	0.00522	0.00166	0.00356	0.00144	6.72	3.17
0.0603	0.00496	0·00142	0.00354	0.00146	5.86	3.23
0.0641	0.00460	0.00125	0.00335	0.00165	6.15	3.21
0.0690	0.00429	0.00108	0.00321	0.00179	6.02	3.22
0.0683	0.00437	0.00110	0.00327	0.00173	5.82	3.23
				Mean value...	6.22	3.21

f. $NaCl + KIO_3 = 0.094—0.102$ m, Na_3 Cit 0.002—0.004 m,
 $\mu = 0,1130—0.1143$.

observed		calculated				
IO_3 M	Ca M	Ca^{++} M	$CaCit^-$ M	Cit^{---} M	$K_{CaCit-}10^4$	pK_{CaCit-}
0.0583	0.00421	0.00122	0.00299	0.00101	4.12	3.38
0.0575	0.00341	0.00126	0.00215	0.00082	4.81	3.32
0.0559	0.00290	0.00134	0.00156	0.00044	3.78	3.42
0.0627	0.00396	0.00106	0.00290	0.00110	4.02	3.39
0.0619	0.00321	0.00108	0.00213	0.00084	4.26	3.37
0.0600	0.00252	0.00115	0.00137	0.00063	5.29	3.28
				Mean value...	4.36	3.36

(4) and (6) μ being computed assuming that both calcium and citrate are fully ionized. The observed calcium is much greater than the one calculated, which means that citrate reduces the activity of calcium. This may be either a general effect of the trivalent ion or a specific effect of the citrate ion. Some experiments were consequently carried out replacing citrate by another trivalent ion, here the cobolticyanid ion. In table III observed and calculated Ca is given as above. The difference throughout is within the experimental error. It is thus a specific effect of the citrate ion and the most likely explanation is that a combination is formed.

The experiments of Table II were then recalculated under the assumption that one mol of calcium combines with one mol of citrate according to scheme (1) and the dissociation constant (2) was then determined. μ was computed assuming that the complex acted as a monovalent ion. In Table IV the experiments of Table II (Table IV b) are given together with a series of other experiments.

At constant ionic strength the constancy of the dissociation constant is fairly good considering the effect of the experimental error. The error of the iodate analysis does not exceed 2 per mil but the error of the calcium analysis may amount to 2 per cent. C_{CaCit^-} is computed from (7) and $C_{Cit^{---}}$ from (8). An error of 2 per cent in total calcium will count heavily on $C_{Cit^{---}}$, and when the values are inserted into (2) the errors will operate in the same direction on K. For example, in Table IV b: $m\,IO_3 = 0.0431$, $m\,Ca = 0.00635$. If $m\,Ca$ is 2 per cent too low, we get $m\,Ca^{++} = 0.00225$, $m\,CaCit^- = 0.00422$, $m\,Cit^{---} = 0.00078$ and $K = 4.16\,10^{-4}$ instead of $4.94\,10^{-4}$. An error in total calcium of 2 per cent here means an error of 20 per cent in K.

In order to see whether the variation of the dissociation

constant with varying ionic strength is within reasonable limits the activity dissociation constant

$$K_{0\,CaCit^-} = \frac{A_{Ca^{++}} \cdot A_{Cit^{---}}}{A_{CaCit^-}} = \frac{C_{Ca^{++}} \cdot f_{Ca^{++}} \cdot C_{Cit^{---}} \cdot f_{Cit^{---}}}{f_{CaCit^-} \cdot C_{CaCit^-}} =$$

$$= K_{CaCit^-} \frac{f_{Ca^{++}} \cdot f_{Cit^{---}}}{f_{CaCit^-}}$$

or

$$pK_{0\,CaCit^-} = pK_{CaCit^-} + pf_{Ca^{++}} + pf_{Cit^{---}} - pf_{CaCit^-}$$

was computed. The following values for the negative logarithms of the activity coefficients were adopted:

$$pf_{Ca^{++}} = 2.016\sqrt{\mu} - 1.58\,\mu$$

$$pf_{Cit^{---}} = 4.536\sqrt{\mu} - 3.89\,\mu$$

$$pf_{CaCit^-} = 0.504\sqrt{\mu} - 0.41\,\mu$$

$pf_{Ca^{++}}$ was taken from KILDE (12), $pf_{Cit^{---}}$ from BJERRUM and UNMACK (14). For the activity coefficient of the complex, no value was known, but as an approximate value the activity coefficient of the primary citrate ion determined by BJERRUM and UNMACK (14) was used. Since the variation in ionic strength is very limited and since it is not known how great an error is committed by substituting the activity coefficient of the primary citrate ion for that of the complex, the pK_0 values of Table V can only be regarded as

Table V.

μ	pK_{CaCit^-}	$pK_{0\,CaCit^-}$
0.0920	3.48	4.84
0.1145	3.37	4.83
0.1328	3.35	4.88
0.1485	3.28	4.85
0.1645	3.21	4.83
	Mean value...	4.85

a rough estimate, but its constancy seems to indicate that no great error has been committed.

The combination of calcium and citrate was then determined at different pH within a range where citric acid is only partly dissociated.

The solutions were made up from sodium chloride, potassium iodate and citric acid and adjusted to different pH with sodium hydroxide. After being saturated with calcium iodate, the solution showed great changes in pH. The hydrogen ion concentration could not be measured with a hydrogen electrode on account of the iodate and a colorimetric method was adopted. The hydrogen ion concentration of the original solution before saturating with calcium iodate was calculated by means of Bjerrum and Unmacks (14) values for the dissociation constants of citric acid. An indicator was added to these solutions and to the solutions after saturating with calcium iodate and the colors were compared. In this way the solutions of known and unknown hydrogen ion concentration were as nearly identical in composition as possible; but even with great care the error in pH amounts to 0.03 (pH means here negative logarithm of the hydrogen ion concentration).

The results of these experiments are put down in Table VI. The concentration of calcium ions, calcium-citrate complex, and free citrate was calculated in the usual manner. By means of the found pH and the dissociation constants of citric acid (Bjerrum and Unmack (14)), the amounts of the free citrate present as undissociated citric acid and as the three ions were calculated. From the concentration of calcium ions and tertiary citrate ions, it is now possible to calculate the concentration of the complex formed by these ions using the above value for the dissociation constant.

Table VI.

Combination of secondary citrate ions and calcium ions

$NaCl + KIO_3 = 0.0900$ m, Citrate 0.005 m, $\mu = 0.1015 - 0.1110$.

IO_3 M	Ca M	pH	Ca^{++} M	Ca Complex M	$HCit^-$ M	Cit^{---} M	$CaCit^-$ M	•CaCit H M	$K_{CaCitH} 10^3$
0.0448	0.00235	3.60	0.00195	0.00040	0.00061	0.000006	0.00003	0.00037	3.2
0.0447	0.00237	3.78	0.00198	0.00038	0.00090	0.000012	0.00006	0.00032	5.6
0.0451	0.00258	3.88	0.00195	0.00063	0.00106	0.000018	0.00009	0.00054	3.8
0.0452	0.00262	4.00	0.00194	0.00068	0.00131	0.000029	0.00015	0.00053	4.8
0.0455	0.00273	4.10	0.00193	0.00080	0.00149	0.000041	0.00021	0.00059	4.9
0.0457	0.00285	4.20	0.00192	0.00093	0.00167	0.000058	0.00029	0.00064	5.0
0.0459	0.00298	4.33	0.00190	0.00108	0.00188	0.000088	0.00043	0.00065	5.5
0.0463	0.00308	4.42	0.00188	0.00120	0.00200	0.000115	0.00055	0.00065	5.8
0.0466	0.00322	4.50	0.00186	0.00136	0.00208	0.000141	0.00066	0.00070	5.5
0.0468	0.00334	4.60	0.00185	0.00149	0.00215	0.000187	0.00088	0.00061	6.5
0.0469	0.00362	4.70	0.00185	0.00177	0.00210	0.000230	0.00106	0.00071	5.5
0.0473	0.00384	4.76	0.00182	0.00202	0.00199	0.000252	0.00115	0.00087	4.2
0.0478	0.00405	4.92	0.00179	0.00226	0.00190	0.000346	0.00153	0.00073	4.7
0.0484	0.00423	5.05	0.00175	0.00248	0.00176	0.00043	0.00185	0.00063	4.9
0.0487	0.00458	5.20	0.00173	0.00275	0.00152	0.00053	0.00224	0.00051	5.2

Mean value.... 5.0

It will be seen that this complex does not account for all the calcium bound there is a surplus of combined calcium. This is assumed to be bound to the secondary citrate ion according to the scheme

$$Ca^{++} + CitH^{--} = CaCitH.$$

The concentration of this complex is to be found in the last column but one of Table VI and the dissociation constant

$$K_{CaCitH} = \frac{C_{Ca^{++}} \cdot C_{CitH^{--}}}{C_{CaCitH}}$$

is given in the last column of the table. Since only a small amount of calcium is bound by the secondary ion and the errors in the different estimations sum up in the estimation of K_{CaCitH} no greater accuracy could be expected.

Discussion.

The above findings are in perfect agreement with the findings of Hastings, Mc Lean, Eichelberger, Hall and Da Costa (10). They find $pK_{CaCit^-} = 3.22$ at $22-23°$ and $\mu = 0.155-0.163$ compared with 3.28 at $\mu = 0.149$ and 3.21 at $\mu = 0.165$ both at $25°$. But as to the formula proposed for the calcium complex

$$\begin{array}{l} CH_2COO^- \\ | \\ C(OH)COO \\ | \qquad\qquad >Ca \\ CH_2COO \end{array}$$
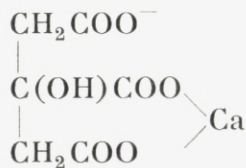
this formula does not emphasize the role that certainly is to be ascribed to the hydroxyl group of citric acid in binding calcium.

In support of the view that the hydroxyl group is eng-
aged in binding the calcium, some findings on tricarbally-
lic acid can be stated. Tricarballylic acid only differs from
the citric acid in having a hydrogen atom in the place of
hydroxyl group.

The experiments were carried out in the same manner
as those with citric acid. The results of the experiments
are to be found in Table VII. It will be seen that though
there is a marked difference between observed and calculated
calcium, this difference is not nearly as great as in the
experiments with sodium citrate (Table II). The dissociation
constant of the complex of calcium and the tricarballylic
ion is consequently much greater than that of the citrate
complex, about 50 times as large.

Table VII.

Observed and calculated concentrations of calcium in
solutions of the sodium salt of tricarballylic acid.

$H_5C_6O_6Na_3$ 0.005 m.   Ionic strength 0.1279—0.1232.

m Ca_{obs} ··········	0.00401	0.00336	0.00245	0.00211	0.00185
m Ca_{cal} ··········	0.00327	0.00273	0.00195	0.00168	0.00144
$K_{CaH_5C_6O}-10^2$ ····	1.87	1.89	1.79	1.78	1.61

It would be of great interest to go into further details
regarding the constitution of the calcium citrate complex;
but with what is known at present, it seems too hazardous
to venture on proposing any formula.

The above quoted investigators likewise determined the
dissociation constant of the complexes formed by citrate ions
and magnesium and strontium ions and found pK_{MgCit}- 3.22
and pK_{SrCit}- 2.70. As a matter of comparison, the dissoci-
ation constant of the complex formed by barium and citrate
was determined. The method was analogous to that used

for calcium. Only a few experiments were carried out, but the pK_{BaCit^-} was found to be approximately 2.69 at $\mu = 0.165$, i. e. nearly the same as that found for strontium citrate.

Summary.

1) In accordance with the hypothesis of Hastings, McLean, Eichelberger, Hall and Da Costa (10), it was assumed that calcium ions react with citrate ions according to the scheme

$$Ca^{++} + Cit^{---} = CaCit^- \cdot$$

2) The experimental findings are in agreement with this scheme of reaction and the dissociation constant

$$K_{CaCit^-} = \frac{C_{Ca^{++}} \cdot C_{Cit^-}}{C_{CaCit^-}}$$

was determined at $25°$ and different ionic strength. At $\mu = 0.165$ pK is found to be 3.21 compared with 3.22 found by the above investigators at $22—23°$ and $\mu = 0.155—0.163$.

3) The pK at zero salt concentration was estimated to 4.85.

4) It was found that calcium also combines with the secondary citrate ion,

$$Ca^{++} + HCit^{--} = CaHCit$$

and the pK for this reaction was determined to 2.3 at $\mu = 0.110$.

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