Complexation of Calcium by α-Isosaccharinic Acid under Alkaline Conditions

Karlien Vercammen,* Martin Alfred Glaus and Luc Robert Van Loon

Laboratory for Waste Management, Paul Scherrer Institute, CH-5232 Villigen, Switzerland

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The complexation of Ca^{2+} by α-isosaccharinic acid (α-ISA) was determined by measuring the solubility of $Ca(\alpha\text{-ISA})_2$ as a function of pH. In the pH range between 12 and 12.8, the observed increase of the total concentration of Ca in solution with increasing pH is explained by the complexation reaction:
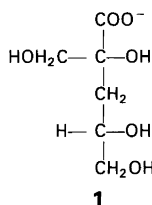
$$Ca^{2+} + \alpha\text{-ISA}^- \rightleftharpoons Ca(\alpha\text{-ISA}_{-H})^0 + H^+$$
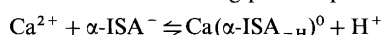
with $\log K^{\circ}_{CaISA^{\circ}} = -10.4$ ($s = 0.2$) at $I = 0$. In addition to this complexation reaction, another complex is postulated:

$$Ca^{2+} + \alpha\text{-ISA}^- \rightleftharpoons Ca(\alpha\text{-ISA})^+$$
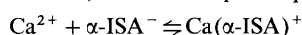
with $\log K^{\circ}_{CaISA^+} = 1.70$. A value for the solubility product of $Ca(\alpha\text{-ISA})_2$ is calculated: $\log K^{\circ}_{sol} = -6.36$ ($s = 0.1$) at $I = 0$.

Organic ligands are inherent components of low-level radioactive waste. Because they can form aqueous radionuclide complexes, they can decrease the sorption of radionuclides on the repository material. Hence, organic ligands might enhance the release of radionuclides from an underground repository to the biosphere. Organic ligands are either present in the waste itself as decontaminating agents (e.g. oxalic, citric acid, EDTA) or they may be formed through the degradation of polymeric organic molecules such as ion-exchange resins,[1] bitumen[2] or cellulose.[3] In addition, organic ligands may originate from cement additives,[4] because cement is commonly used for solidification and encasement of waste and for the construction of the underground caverns of the repository.

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                COO⁻
                |
   HOH₂C—  C—OH
                |
                CH₂
                |
   H—  C—OH
                |
                CH₂OH
                1
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Several studies have shown that α-isosaccharinic acid (α-ISA, 1), formed by the alkaline degradation of cellulose,[5,6] has a large effect on the sorption and solubility of radionuclides[3,7,8] such as Eu^{III}, Th^{IV} and Pu^{IV}. Sorption decreases and solubility increases in the presence of α-ISA. It has further been shown that the com-

plexation of radionuclides in an alkaline solution of degraded cellulose is dominated by α-ISA.[3] Substantial amounts of the organic waste present in a repository for low- and intermediate-level waste in Switzerland are cellulosic. It may therefore be hypothesised that α-ISA is among the most important organic compounds present in a repository, with respect to the complexation of radionuclides. However, no direct evidence for complex formation between radionuclides and α-ISA exists.

This study is the first in a series of investigations into the complexation behaviour of α-ISA, and focuses on complexation with Ca^{2+}. Owing to the presence of portlandite in cement, the concentration of Ca^{2+} in the pore water of a cementitious repository is relatively high (in the mM range) compared to the concentration of radionuclides (in the nM range). Therefore, Ca^{2+} could compete with these radionuclides for complexation with α-ISA, even if its affinity for α-ISA were orders of magnitude lower than that of radionuclides. In addition, Ca^{2+} might promote the complexation of radionuclides by α-ISA through formation of ternary complexes. This was recently shown for complexation of Al^{3+} by structurally related polyhydroxy carboxylic acids[9] in the presence of Ca^{2+}.

In general, the complexation of multivalent metal ions by polyhydroxy carboxylates (L^-) can involve the carboxylate group and/or deprotonated hydroxo groups as ligand sites. The stoichiometry of the formation of a 1:1 complex is represented by the following equation:

$$M^{z+} + L^- \rightleftharpoons ML^{z-n-1}_{-nH} + nH^+ \tag{1}$$

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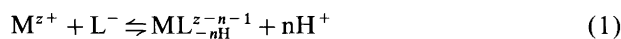
*To whom correspondence should be addressed.

According to a generalised coordination–ionisation scheme postulated for polyhydroxy carboxylic acids,[10] n is expected to be 0 for the binding of Ca^{2+} in the pH region 4–10, whereas at pH > 10, n is expected to be 1. With a single exception,[11] only reactions without proton exchange ($n = 0$) are described in the literature.[12–18]

Almost nothing is known about the complexation of Ca^{2+} by α-ISA. Indirect evidence for such a reaction has recently been given by Van Loon and Glaus[3] in a study of the degradation of cellulose in artificial cement pore water (pH 13.3, 2 mM Ca). It was found that the total concentration of Ca in solution increased with increasing degree of degradation of cellulose, i.e. with increasing concentration of α-ISA. In the same study, the sorption of α-ISA on cement was measured, and the same dependency of the total Ca concentration on the concentration of α-ISA was found. The total concentrations of Ca observed were significantly larger than could be explained from the solubility of $Ca(OH)_2$. However, by postulating the formation of a 1 : 1 complex between Ca^{2+} and α-ISA with $n = 1$, the authors could satisfactorily explain the experimental data.

The aim of the present work was to verify the existence of such an uncharged $Ca(\alpha\text{-ISA}_{-H})^0$ complex in a well defined system. Owing to the heterogeneity of the experimental systems investigated by Van Loon and Glaus,[3] alternative explanations were possible for the increased Ca concentrations. For example, the involvement of other degradation products could not be excluded. Further, all these experiments were performed at a pH of 13.3. For the present study, solubility experiments with the sparingly soluble $Ca(\alpha\text{-ISA})_2$ at various alkaline pH values between 10.5 and 13.3 are performed. If a $Ca(\alpha\text{-ISA}_{-H})^0$ complex is formed, then the total concentration of Ca is expected to be dependent on pH owing to the exchange of one proton according to eqn. (1).

Materials and methods

Synthesis of $Ca(\alpha\text{-ISA})_2$. The original procedure described by Whistler and BeMiller[19] was slightly modified. 200 g of lactose monohydrate (Merck) and 54.4 g of calcium hydroxide (Fluka) were dissolved in 2 l of argon-flushed water and stored at room temperature for 3 days in a closed vessel. After this time, the mixture was boiled for 6 h, keeping the volume constant by adding small amounts of water. The hot solution was filtered, and the volume of the filtrate reduced to about 370 ml by boiling. The solution, containing a precipitate of $Ca(\alpha\text{-ISA})_2$, was stored at 4 °C overnight. The precipitate was removed by filtration, washed with water and ethanol, and dried overnight in a vaccuum oven at 50 °C. The crude product was redissolved by boiling at a ratio of 1.2 g of the crude product to 100 g of water. After insoluble impurities had been removed from the hot solution by filtration, the volume was reduced to ca. 10% of the starting volume. The white precipitate formed was washed with water and ethanol and dried overnight in a

vacuum oven at 50 °C. HPLC analysis on a Carbopac PA-100 column (Dionex, amperometric detection using a gold working electrode) showed the presence of two peaks in the $Ca(\alpha\text{-ISA})_2$ salt. The peak area of α-ISA contributed to 98% of the total peak area.

Solubility experiments: general procedure. All the solubility experiments were performed in a glovebox under N_2 atmosphere (O_2, $CO_2 < 5$ ppm) and at 25 ± 2 °C.

Approximately 0.5 g of $Ca(\alpha\text{-ISA})_2$ was equilibrated with 20 ml of an alkaline stock solution in a 40-ml polyallomere centrifuge tube. The stock solutions contained NaOH and $NaClO_4$ in amounts such that a total ionic strength of 0.3 M resulted at the desired pH between 10.8 and 13.3. In some experiments, small amounts (0.05–0.15 g) of $Ca(OH)_2$ were also added. The tubes were shaken end-over-end for well-defined times between 1 day and 2 weeks. After shaking, the solution was filtered (0.45 μm, non-sterile Acrodisc filter, polysulfone membrane, Gelman Sciences), and the filtrate was analysed for Ca by ICP–AES and for α-ISA by ion chromatography (Dionex DX-500, Carbopac PA-100 4 × 250 mm, eluent 0.08 M NaOH. flow 1 ml min^{-1}, detection by suppressed conductivity). Note that no significant difference in the analytical results was obtained by centrifuging the samples (27 000g, 0.5 h) instead of filtering.

pH Measurements. pH was measured using a glass electrode (ORION, ROSS Combination pH electrode). The glass electrode was calibrated by adding suitable amounts of 0.3 M NaOH to an aliquot of 0.3 M $NaClO_4$. The pH in these calibration solutions was calculated as follows:

$$pH = 14 + \log_{10} a_{OH} \tag{2}$$

where a_{OH} is the activity of hydroxide. Activity coefficients (γ_i) of an ion i in solution were calculated using the Davies equation valid for 25 °C:[20]

$$\log \gamma_i = -0.5 z_i^2 \left(\frac{I^{1/2}}{(1 + I^{1/2})} - 0.3 I \right) \tag{3}$$

where z_i is the charge of ion i and I is the ionic strength of the solution. The relation between pH and potential in the pH region from 10.5 to 13 showed a slight deviation from linear behaviour and was fitted by a second-order polynomial function. Possible drift of the electrode with time was controlled by repeating the calibration procedure after time intervals of approximately 2 h.

Modelling of chemical equilibria. The fitting of complexation constants or equilibrium concentrations to a given set of experimental data was performed using the PHREEQE geochemical code.[21] This program uses the Davies equation [eqn. (3)] to calculate activity coefficients. Thermodynamic equilibrium constants used by the program are specified in the text where necessary.

Results and discussion

Kinetics. To determine the time required to equilibrate the $Ca(\alpha\text{-ISA})_2$–$NaOH/NaClO_4$ suspensions, the supernatants were analysed after times varying between 1 and 14 days. The results are shown in Fig. 1.

For pH values below pH 12.8, no differences in the total concentration of Ca are observed after the equilibrium times studied. Beyond pH 12.8, two different situations can be distinguished. In the short term (1–2 days) a continuous increase of the total concentration of Ca is observed with increasing pH, whereas at longer times (3–14 days) the total concentration of Ca reaches a maximum value at a pH of approximately 12.8 and decreases at higher pH values. Obviously, in the short term the system is not in equilibrium. The fact that the total concentration of Ca suddenly drops between 2 and 3 days suggests that a new solid phase is formed which is less soluble than $Ca(\alpha\text{-ISA})_2$. Presumably this solid phase is portlandite, because the solubility of portlandite is strongly pH dependent. With increasing pH this solubility decreases owing to the reaction

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2\,OH^- \tag{4}$$

Thus it can be hypothesised that in the short term the systems are oversaturated with respect to portlandite. Only one single data point (pH 13.2; 7 days) deviates from this behaviour. In this system, the formation of the new solid phase seems to be delayed for unknown reasons.

To check the hypothesis of portlandite precipitation, two different systems were set up. The first contained only $Ca(\alpha\text{-ISA})_2$, whereas the second also contained small amounts of $Ca(OH)_2$. Both systems were equilibrated with a $NaOH/NaClO_4$ mixture at pH 13.3 and $I = 0.3$ M for times of 1 day and 1 week. The results are given in Table 1. According to the hypothesis of delayed precipitation of portlandite, it would be expected that the $Ca(OH)_2$ initially present would be a source of nucleation cores for the precipitation of portlandite. Consequently, the total concentration of Ca in the short
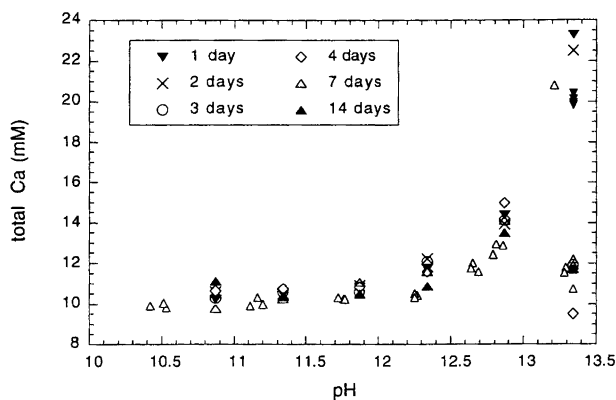

Fig. 1. Total concentration of Ca in solutions in equilibrium with $Ca(\alpha\text{-ISA})_2$ determined as a function of pH and equilibration time.

Table 1. Composition of solution in equilibrium with $Ca(\alpha\text{-ISA})_2$ at pH 13.3, in systems without and with initial addition of $Ca(OH)_2$ ($I = 0.3$ M, $T = 25\,^\circ$C).

Equilibration time	Ca(α-ISA) Total Ca /mM	Total α-ISA /mM	Ca(α-ISA)₂ and Ca(OH)₂ Total Ca /mM	Total α-ISA /mM
1 day	20.0	44.4	9.6	53.5
	$N^a = 5$	$N = 5$	$N = 5$	$N = 5$
	$s^b = 0.3$	$s = 0.2$	$s = 0.3$	$s = 0.5$
1 week	11.6	48.6	10.0	53.4
	$N = 4$	$N = 4$	$N = 5$	$N = 4$
	$s = 0.6$	$s = 1.2$	$s = 0.9$	$s = 1.8$

$^a N$, number of data. $^b s$, standard deviation.

term should be lower than in a system without $Ca(OH)_2$ initially present. Once the Ca concentration decreases due to the precipitation of portlandite, the concentration of α-ISA concomitantly increases in order to maintain saturation of the solution with respect to $Ca(\alpha\text{-ISA})_2$. Thus, it is to be expected that the concentration of α-ISA in the short term would be higher in the system with $Ca(OH)_2$ initially present. As can be seen from Table 1, the results for Ca and α-ISA are in agreement with the hypothesis of delayed precipitation of portlandite. Furthermore, after 1 week of equilibration, the samples with and without initial $Ca(OH)_2$ show only a small difference in total Ca concentrations. Considering the uncertainties indicated, it is likely that this small difference is within experimental uncertainty.
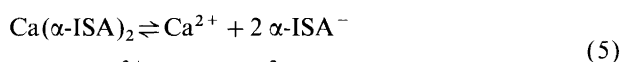
Summarising, it can be concluded that the systems equilibrated for 3 days or more are at equilibrium with $Ca(OH)_2$, so that these results may be used for the thermodynamic modelling of the chemical equilibria involved.

Modelling of the chemical equilibria involved. The increase in the total Ca concentration between pH 12 and 12.8 (shown in Fig. 1) is evidence for the formation of a complex between Ca^{2+} and α-ISA, according to eqn. (1) with $n \geq 1$. Because the formation of such complexes involves the dissociation of protons, the degree of complexation progresses with increasing pH, and consequently the concentration of Ca in solution increases. If the total concentration of Ca in solution were governed only by the solubility of $Ca(\alpha\text{-ISA})_2$ and $Ca(OH)_2$, no increase in the total concentration of Ca would be expected. Up to pH 12.8 the total concentration of Ca would be constant, because it is dominated by the dissolution of $Ca(\alpha\text{-ISA})_2$, a pH-independent process. Beyond pH 12.8, the concentration of Ca in solution will decrease because of the precipitation of $Ca(OH)_2$, which is pH-dependent [cf. eqn. (4)].

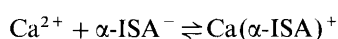As can be seen from Fig. 1, $Ca(\alpha\text{-ISA})_2$ systems in equilibrium with $Ca(OH)_2$ at pH 13.3 have a total Ca concentration of about 10 mM. On the other hand, if $Ca(\alpha\text{-ISA})_2$ were absent, the dissolution of $Ca(OH)_2$

alone at pH 13.3 would lead to a Ca concentration of about 2 mM. The higher Ca concentration obtained is caused by the formation of a $Ca(\alpha\text{-ISA}_{-nH})^{1-n}$ complex with $n \geqslant 1$.

In the following, the aim is to describe the experimental data with a minimum set of equilibrium reactions for α-ISA. Those reactions for which the stability constants are known from the literature are summarized in Table 2. Those for which no thermodynamic data are available are shown as eqns. (5)–(7) along with their associated equilibrium constants (braces indicate activities):

$$Ca(\alpha\text{-ISA})_2 \rightleftharpoons Ca^{2+} + 2\,\alpha\text{-ISA}^-$$

$$K_{sol}^\circ = \{Ca^{2+}\}\{\alpha\text{-ISA}^-\}^2 \tag{5}$$

$$Ca^{2+} + \alpha\text{-ISA}^- \rightleftharpoons Ca(\alpha\text{-ISA})^+$$

$$K_{CaISA^+}^\circ = \frac{\{Ca(\alpha\text{-ISA})^+\}}{\{Ca^{2+}\}\{\alpha\text{-ISA}^-\}} \tag{6}$$
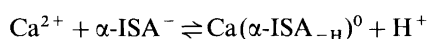
$$Ca^{2+} + \alpha\text{-ISA}^- \rightleftharpoons Ca(\alpha\text{-ISA}_{-H})^0 + H^+$$

$$K_{CaISA^0}^\circ = \frac{\{Ca(\alpha\text{-ISA}_{-H})^0\}\{H^+\}}{\{Ca^{2+}\}\{\alpha\text{-ISA}^-\}} \tag{7}$$

The reason for the including complexation reaction (6) [involving $n=0$, cf. eqn. (1)] is the chemical analogy of

Table 2. Chemical equilibria and corresponding thermodynamic constants used ($I=0$, $T=25\,^\circ$C).

Reaction	log K	Ref.
$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2\,OH^-$	−5.2	22
$Ca^{2+} + H_2O \rightleftharpoons CaOH^+ + H^+$	−12.8	23
$H_2O \rightleftharpoons H^+ + OH^-$	−14.0	23

α-ISA with structurally related polyhydroxy carboxylates, for which such reactions have been described in the literature.[12–18]

In view of the structural analogy between gluconate and α-ISA, log $K_{CaISA^+}^\circ$ is set to 1.7, assuming that $K_{CaISA^+}^\circ$ equals the corresponding equilibrium constant for gluconate.[18] Note that this value is comparable with the equilibrium constants of structurally related ligands. In Table 3 these ligands and the equilibrium constants (K_1) corresponding to the formation of their 1:1 complexes with Ca^{2+} are shown.

With a fixed value for $K_{CaISA^+}^\circ$ the solubility product of $Ca(\alpha\text{-ISA})_2$ can be found using the experimental data obtained between pH 10.8 and 12. In this pH range, the concentration of total Ca in solution does not depend on pH (cf. Fig. 1). Therefore, the hypothesis that the complexation reaction involving $n=1$ [cf. eqn. (1)] plays a negligible role could be valid, and hence K_{sol}° is the only unknown parameter. The optimal value for log K_{sol}° is determined as follows. For different values of K_{sol}°, the concentration of total Ca in solution is calculated at every measured pH. This Ca concentration is compared with the measured one. The value for K_{sol}° that leads to the minimum sum of squares of the differences of calculated and measured Ca concentrations is chosen as the best value to describe the experimental data points $\{\Sigma([Ca]_{calc} - [Ca]_{meas})^2\}$. This procedure results in log $K_{sol}^\circ = -6.36 \pm 0.1$. The uncertainty ($\pm 0.1$) is not a standard deviation, but represents an uncertainty range of log K_{sol}° by which the most important experimental points are covered.

Finally, with fixed values for log $K_{CaISA^+}^\circ$ and K_{sol}°, an optimal value for $K_{CaISA^0}^\circ$ can be found from the experi-

Table 3. (Poly)hydroxycarboxylic acids (PHL) and their corresponding equilibrium constants for the formation of a Ca(PHL)$^+$ complex ($I=0$ M, $T=25\,^\circ$C).

Ligand	Molecular structure	log K_1	Ref.
Glycolic acid	HO—CH$_2$ \ COOH	1.59 1.62^a 1.65	12 13^b 14
Lactic acid	COOH | CH HO CH$_3$	1.42 1.46^a 1.47 1.55 1.57^a	15 16 12 17 13^b
Glyceric acid	COOH | CH OH HO C H$_2$	1.69^a	13^b
Gluconic acid	H$_2$ H$_2$ C C COOH HOH$_2$C C C H$_2$ H$_2$	1.59^a 1.70^a 1.72^a	16 18 13^b

^{a}Recalculated for $I=0$ M using the Davies equation [eqn. (3)]. ^{b}No temperature specified.

mental data in the pH range 12–13.3. The value for $\log K^\circ_{CaISA^0}$ is determined by the same least-squares procedure as for $\log K^\circ_{sol}$ and results in $\log K^\circ_{CaISA^0} = -10.4 \pm 0.2$. In Fig. 2 the effect of the uncertainty on $\log K^\circ_{CaISA^0}$ is shown by the shaded area.

A summary of the optimum values for the three equilibrium constants associated with eqns. (5)–(7) is given in Table 4. The value for $\log K^\circ_{sol}$ is in good agreement with one measured at neutral pH ($\log K^\circ_{sol} = -6.53$).[24] Also, the value found for $\log K^\circ_{CaISA^0}$ agrees well with the one estimated in Ref. 3 ($\log K^\circ_{CaISA^0} = -10.50$) and is similar to values for the uncharged complexes between Ca^{2+} and galacturonic or glucuronic acid at an ionic strength of 1 M: $\log K^\circ_{CaGal^0} = -10.15$ or $\log K^\circ_{CaGluc^0} = -10.40$, respectively.[11]

A comparison between the Ca data measured between pH 10.5 and 13.3 and the model proposed (Tables 2 and 4) is shown by the solid line in Fig. 2. As this figure shows, the model simulates the experimental data well except for the data at pH 13.3. The data at this pH can be fitted better if the value for $\log K^\circ_{CaISA^0}$ is changed to -10.2 (upper limit in Fig. 2). In this case, however, the model fits the data between pH 12 and 13 less well.

When $Ca(\alpha\text{-ISA})_2$ is equilibrated in a $NaClO_4/NaOH$ solution for only a short time (1–2 days), the precipita-

tion of $Ca(OH)_2$ does not seem to take place (cf. Fig. 1). To test this hypothesis, a simulation was made omitting the $Ca(OH)_2$ equilibrium in the modelling. The result of this simulation is shown in Fig. 2 as a broken line. The good agreement between the experimental data and the model confirms the hypothesis of a system oversaturated with respect to $Ca(OH)_2$, and is another indication for the validity of the complexation constants shown in Table 4.

The assumption of a pH-dependent complexation reaction with $n \geqslant 1$ [cf. eqn. (1)] is based on the generalised coordination–ionisation scheme.[10] This scheme generally predicts the stoichiometry of the complexes formed between a polyhydroxy ligand and a given metal ion as a function of pH. For Ca^{2+} the number of protons dissociated from hydroxyl groups at pH > 10 is predicted to be 1. The question arises as to whether models including complexation reactions with values for n different from one, are also able to describe the experimental data. Therefore, two other complexation models were also tested: one including only the complexation reaction with $n = 0$ (model A) and another including, in addition, a complexation reaction with $n = 2$ (model B). An overview of the complexation reactions tested is given in Table 5. The equilibrium constant for the complexation reaction with $n = 0$ is set to 1.7 in accordance with the model proposed (Table 4). The results are shown in Figs. 3 and 4. In contrast to the model proposed, the alternative model A is not able to describe the increase in the total Ca concentration because a pH-dependent complexation reaction is absent (Fig. 3).

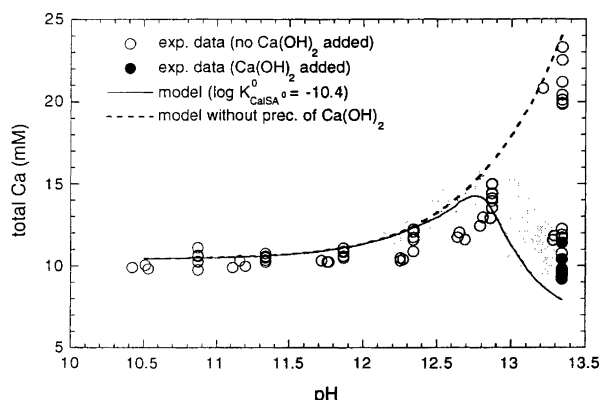For the alternative model B, the complexation con-

Fig. 2. Comparison between the experimental Ca data (1–14 days) and the model proposed to simulate these data. The full line represents the model based on Tables 2 and 4. The variation of the model between the upper limit $\log K^\circ_{CaISA^0} = -10.2$ and the lower limit $\log K^\circ_{CaISA^0} = -10.6$ is given by the shaded area. The broken line shows the same model not taking $Ca(OH)_2$ precipitation into account.

Table 4. Overview of the equilibrium constants ($I = 0$ M, $T = 25\,^\circ C$) proposed to simulate the interaction between Ca^{2+} and α-ISA.

	log K	
Reaction	Average	Uncertainty
$Ca^{2+} + \alpha\text{-ISA}^- \rightleftharpoons Ca(\alpha\text{-ISA})^+$	1.70	—
$Ca(\alpha\text{-ISA})_2 \rightleftharpoons Ca^{2+} + 2\,\alpha\text{-ISA}^-$	−6.36	0.1
$Ca^{2+} + \alpha\text{-ISA}^- \rightleftharpoons Ca(\alpha\text{-ISA}_{-H})^0 + H^+$	−10.4	0.2

Table 5. Overview of alternative complexation models tested.

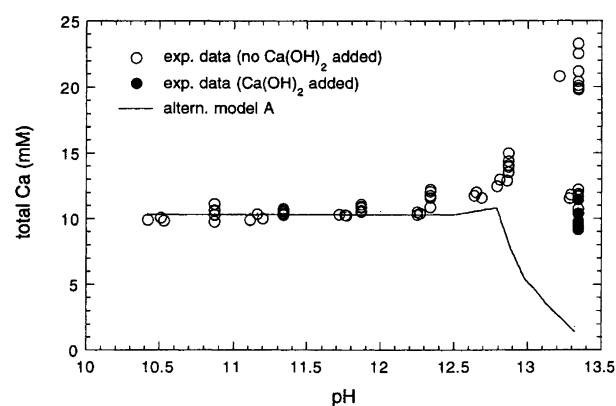| Equilibrium reactions	Model A	Model B
$Ca(\alpha\text{-ISA})_2 \rightleftharpoons Ca^{2+} + 2\,\alpha\text{-ISA}^-$	−6.36	−6.36
$Ca^{2+} + \alpha\text{-ISA}^- \rightleftharpoons Ca(\alpha\text{-ISA})^+$	1.7	1.7
$Ca^{2+} + \alpha\text{-ISA}^- \rightleftharpoons Ca(\alpha\text{-ISA}_{-2H})^- + 2\,H^+$		−23.80

Fig. 3. Comparison between the experimental Ca data and the alternative model A, which includes only the complexation reaction between Ca^{2+} and α-ISA with $n = 0$ in eqn. (1).
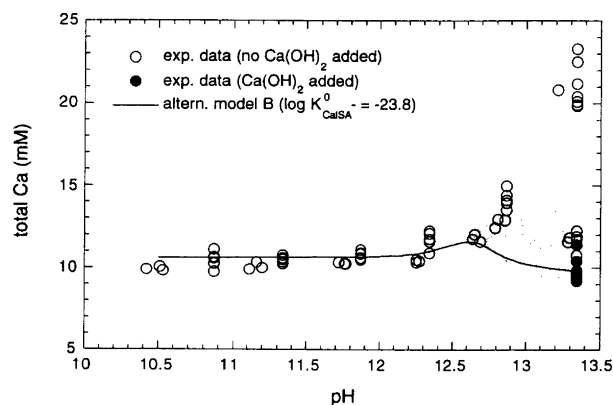
Fig. 4. Comparison between the experimental Ca data and the alternative model B, which includes complexation reactions between Ca^{2+} and α-ISA with $n=0$ and $n=2$ in eqn. (1). The variation of the alternative model B between the upper limit $\log K^{\circ}_{CaISA^-} = -23.5$ and the lower limit $\log K^{\circ}_{CaISA^-} = -24.0$ is given by the shaded area.

stant K_{CaISA^-} in Table 5 is derived by a least-squares method. With $\log K_{CaISA^-} = -23.8$, the experimental data can be simulated, but with no significant improvement compared to the model proposed. It can not be concluded that this alternative model B is worse than the model proposed. However, since it is unlikely that Ca^{2+} is able to displace two protons from α-ISA, the model proposed in Table 4 is preferred.

Conclusion

A model for the complexation of Ca^{2+} by α-ISA at alkaline pH has been proposed. At $pH < 12$, a $Ca(\alpha$-ISA$)^+$ complex is formed without deprotonation of a hydroxylic group. At $pH > 12$, a proton of a hydroxylic group is displaced by Ca^{2+}, and an uncharged $Ca(\alpha$-ISA$_{-H})^0$ complex is formed. The model proposed here is in agreement with the general coordination–ionization scheme for polyhydroxy carboxylic acids[10] and is the first experimental evidence for the validity of this scheme for Ca^{2+}. Moreover, the existence of the $Ca(\alpha$-ISA$_{-H})^0$ complex is confirmation of a model proposed earlier.[3]

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