Stability of the Ion Pair Between Ca²⁺ and 2-(Hydroxymethyl)-3-Deoxy-D-*erythro*-Pentonate (α-Isosaccharinate)

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Ion-pair formation between Ca^{2+} and α-isosaccharinate, $Ca^{2+} + ISA^- \rightleftharpoons CaISA^+$, was studied by two independent methods: an ion-exchange and a potentiometric method (Ca-selective electrode). The two methods gave similar values for the complexation constant, $\log K^o_{CaISA^+}$ at $I = 0$, $(22 \pm 1)°C$. The ion-exchange method gave a value of $\log K^o_{CaISA^+} = (1.8 \pm 0.1)$ and the potentiometric method resulted in $\log K^o_{CaISA^+} = (1.78 \pm 0.04)$. These values are in good agreement with the estimated value, $\log K^o_{CaISA^+} = 1.7$, based on the formation of a Ca-gluconate ion pair.

1. INTRODUCTION

The alkaline degradation of cellulose is an important process that can have an adverse effect on the safety of a cementitious radioactive waste repository.[1] One of the main degradation products formed by this process is 2-(hydroxymethyl)-3-deoxy-D-erythro-pentonic acid,[2] also referred to as α-isosaccharinic acid (abbreviated as ISA, if the protonation state of the compound is not of importance). ISA is a polyhydroxy type of ligand (Fig. 1) and forms stable aqueous complexes with several radionuclides.[3–5] It might, therefore, increase their solubility and/or decrease their sorption on cement[6] resulting in an enhanced release of radionuclides from an underground repository to the biosphere. These effects

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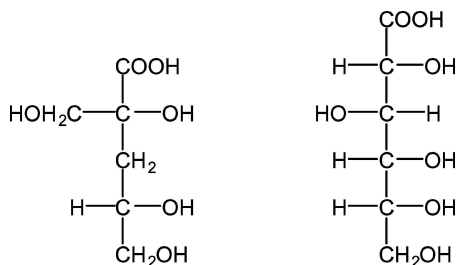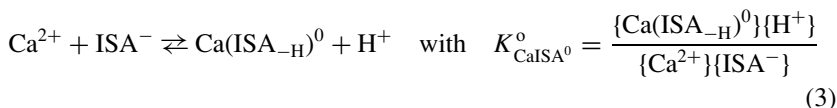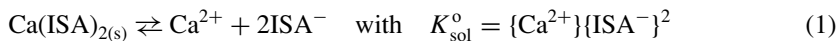[2]Infraserv GmbH & Co. Höchst KG, DE-65926 Frankfurt am Main, Germany.

Fig. 1. Structures of α-isosaccharinic acid (left) and
gluconic acid (right).

depend mainly on the concentration of ISA in the pore water of a repository.[7] The concentration depends on several factors, among which are the formation of soluble complexes and sparingly soluble salts with Ca^{2+}. According to a previous study,[8] the chemical equilibria relevant to calculating the total Ca concentration in solution are (K_i^{o} are the stability constants valid for zero ionic strength and the braces indicate the activities of the species):

$$Ca(ISA)_{2(s)} \rightleftarrows Ca^{2+} + 2ISA^- \quad \text{with} \quad K_{sol}^{o} = \{Ca^{2+}\}\{ISA^-\}^2 \tag{1}$$

$$Ca^{2+} + ISA^- \rightleftarrows Ca(ISA)^+ \quad \text{with} \quad K_{CaISA^+}^{o} = \frac{\{Ca(ISA)^+\}}{\{Ca^{2+}\}\{ISA^-\}} \tag{2}$$

$$Ca^{2+} + ISA^- \rightleftarrows Ca(ISA_{-H})^0 + H^+ \quad \text{with} \quad K_{CaISA^0}^{o} = \frac{\{Ca(ISA_{-H})^0\}\{H^+\}}{\{Ca^{2+}\}\{ISA^-\}} \tag{3}$$

The stability constants involved in Eqs. (1–3) have been evaluated in several works, in which the solubility of sparingly soluble $Ca(ISA)_{2(s)}$ was investigated as a function of pH[8–10] and/or total concentration of ISA. It has been hypothesized that the $Ca(ISA)^+$ and $Ca(ISA_{-H})^0$ complexes are ion pairs. The formation of $Ca(ISA)^+$ complexes is pH independent, whereas formation of $Ca(ISA_{-H})^0$ complexes becomes only noticeable at pH > 11.[8] It has to be noted that the values obtained for the stability constants involved in Eqs. (1) and (2) cannot readily be determined independently of each other from solubility studies of $Ca(ISA)_{2(s)}$, because the effect of the complexation reaction (2) is comparatively weak. For this reason, the value of $K_{CaISA^+}^{o}$ obtained from solubility measurements of $Ca(ISA)_{2(s)}$ is strongly correlated with the solubility product of $Ca(ISA)_{2(s)}$. In order to avoid such problems, the value of $K_{CaISA^+}^{o}$ has been assumed in previous work[8,9] to be equal—by chemical analogy—to the stability constant for the Ca-gluconate$^+$ ion pair (log $K_{CaISA^+}^{o} = 1.7$). Although there are some data available from literature for ion-pair formation between Ca and (poly)hydroxycarboxylic acids,[8] the validity of chemical analogy cannot readily be predicted. For this reason it is strongly

desirable for $K^o_{CaISA^+}$ to be measured in the absence of solid Ca(ISA)$_{2(s)}$, which would thus yield a value independent of K^o_{sol}. This study describes such measurements. Two independent methods were used, *i.e.*, an ion-exchange method and a method using a Ca ion-sensitive electrode (CSE). Both methods can be applied at Ca^{2+} concentrations well below the solubility product of Ca(ISA)$_{2(s)}$.

2. MATERIALS AND METHODS

2.1. General

Ultra-pure water ($R = 18.2$ MΩ) was prepared by ultrafiltration with a Milli-Q$^®$ water purification system (Millipore, Bedford, MA, USA). Reagents of the highest purity were obtained from Fluka (Buchs, Switzerland) or Merck (Dietikon, Switzerland). The sodium salt of ISA was prepared according to previous work.[2] The pH was measured on a WTW microprocessor 535 pH meter using a combined glass electrode (Ingold, Switzerland). Calibration of the electrode was carried out using Titrisol buffers in the appropriate pH range (Merck, Switzerland).

2.2. Ion Exchange Method

2.2.1. Theoretical Background

The ion-exchange method was originally designed to determine the stability constants of a ML complex by measuring the solid/liquid distribution coefficients (the amount of *M* sorbed divided by its total concentration in solution) of the metal M in the absence (K^o_d) and presence (K_d) of different concentrations of the ligand L.[11–13] The dependence of K_d on the ligand concentration gives information on the stoichiometry of the complexation reactions and the stability constants involved. For the formation of 1:1 *ML* complexes in solution:

$$M + L \rightleftarrows ML \quad \text{with} \quad K_{ML} = \frac{[ML]}{[M] \cdot [L]} \tag{4}$$
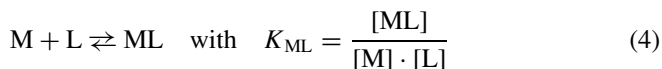
the dependence of K_d on the ligand concentration [L] can be written as:

$$K_d = \frac{K^o_d}{1 + K_{ML} \cdot [L]} \tag{5}$$

where brackets denote molar concentrations (mol-dm^{-3}) of the species in solution and: K^o_d = distribution coefficient of M in the absence of L (dm^3-kg^{-1}), K_d = distribution coefficient of M in the presence of L (dm^3-kg^{-1}), K_{ML} = conditional stability constant for the experimental ionic strength.

The method ordinarily uses trace-metal concentrations (where radioactive tracers are convenient) and a constant ionic strength medium. It can be applied

only when the complex formed does not adsorb on the ion-exchange resin. It has been shown in the literature[14] that 1:1 complexes of bivalent cations with single negatively charged anions did not absorb on similar types of cation exchangers as used in this work.

2.2.2. Experimental

An amount of 10 g of a wet Dowex 50 W X-4 cation exchange resin in the H^+-form was converted into the Na^+ form by washing the resin twice with 250 cm^3 of 0.1 M NaOH and equilibrating three times with 0.1 M $NaClO_4$. After equilibration, the resin was washed with demineralized water and dried at 50°C. Portions of 100 mg of the resin were transferred to 50 cm^3 centrifuge tubes. 30 cm^3 portions of a solution containing $NaClO_4$, 1 mM buffer (morpholinoethanesulfonic acid), and ISA in a concentration range between 0 and 0.1 M were added. The pH of the solutions was adjusted to (6.0 ± 0.1), and the total ionic strength was 0.2 M. The solutions were spiked with 20 μl of a ^{45}Ca tracer solution. The suspensions were shaken end-over-end for 24 h at a temperature of $(22 \pm 1)°C$. After sedimentation of the resin, a 1 cm^3 sample was withdrawn from the clear supernatant and assayed for ^{45}Ca with a liquid scintillation counter (Tricarb 2500, Packard-Canberra) using Ultima Gold^{TM} as a scintillation cocktail. From the difference in radioactivity in solution before and after equilibrium, the distribution coefficient was calculated:

$$K_d = \frac{(A_{in} - A_{eq})}{A_{eq}} \cdot \frac{V}{W} \tag{6}$$

with: A_{in} = the radioactivity of ^{45}Ca in the suspension (cpm-dm^{-3}), A_{eq} = the radioactivity of ^{45}Ca in the supernatant solution (cpm-dm^{-3}), V = volume of the suspension (dm^3), W = mass of the resin (kg), and cpm denotes counts per minute.

2.3. Ca Ion-Selective Electrode

2.3.1. Theoretical Background

For a simple thermodynamic equilibrium as described by Eq. (4), knowledge of the concentration of the free metal aqua ion in a given system with known total concentrations of the metal ion, $[M]_{tot}$, and the ligand, $[L]_{tot}$, allows for the calculation of K_{ML} to be made. Through the mass balance for M

$$[M]_{tot} = [M] + [ML] \tag{7}$$

the concentration of ML can be determined. Further, if the experimental system is designed such that the ligand is present at a large excess compared to the metal ion, the concentration of the free ligand, [L], can be approximated from $[L]_{tot}$. K_{ML}, which is valid for the experimental ionic strength, can then be calculated

according to the relation:

$$K_{ML} = \frac{([M]_{tot} - [M])}{[M] \cdot [L]_{tot}} \tag{8}$$

For the present purpose the concentration of free Ca^{2+} was measured using a calcium-specific electrode (CSE) in combination with a Ag/AgCl reference electrode. The Ca^{2+} concentration can be calculated from the electromotive force (E) and the previously determined calibration parameters of the electrode. The calibration of the electrode is based on the Nernstian equation,[15]

$$E = E° + \frac{2.303 \, RT}{2 \, F} \log[Ca^{2+}] \tag{9}$$

and is achieved by addition of known amounts of Ca^{2+} to the background electrolyte used for the titration, where F is the Faraday constant, R is the universal gas constant, T represents the absolute temperature, and $[Ca^{2+}]$ is the concentration of Ca^{2+}. The calibration parameters, $E°$ (intercept) and $2.303RT/2F$ (slope) are obtained from linear regression. $E°$ is combined parameter, which incorporates not only the standard reduction potential of the electrode, but also other constant terms, such as the liquid junction potential, the activity coefficient of Ca^{2+} and others.

2.3.2. Experimental

25 cm^3 of a solution containing 0.2 M NaCl and 1 mM of morpholinoethane-sulfonic acid (buffered to pH 6) were added to a closed titration vessel equipped with a CSE (Metrohm, Switzerland), an Ag/AgCl reference electrode (Metrohm, Switzerland) and a combined pH electrode. The temperature was kept at (22 ± 1)°C. To this solution, 0.1 M Ca(NO$_3$)$_2$ (standardized against an EDTA solution of known concentration) was added stepwise to obtain a series of Ca concentrations between 0.01 and 0.1 mM. The potential read after each addition was used to calibrate the CSE. Subsequently, known increments of a NaISA solution (0.86 M) were added to cover an ISA concentration range between 4 and 80 mM. The slight changes in pH caused thereby were corrected by addition of suitable amounts of HCl, *i.e.*, the pH was kept at (6.1 ± 0.2). Each experiment was finished by checking the calibration parameters by a separate recalibration of the electrode. Upon finding discrepancies in calibration parameters of more than 1%, the titration results were discarded.

For each addition of ISA the potential of the CSE (E) was read and transformed to the concentration of Ca^{2+} using the relation,

$$\log[Ca^{2+}] = \frac{E - E°}{s} \tag{10}$$

where s is the slope ($s = 2.303RT/2F$).

Because the ionic strength increased from 0.2 M to $\sim$0.26 M during the addition of ISA, the influence of ionic strength on the calibration parameters was separately tested for ionic strengths between 0.2 and 0.3 M. It turned out that for the calculation of K_{ML} the dependence of the calibration parameters on ionic strength could be neglected in this range.

3. RESULTS AND DISCUSSION

3.1. Ion-Exchange Method

Figure 2 shows the K_d values of ^{45}Ca as a function of the total ISA concentration in the equilibrium solution. With increasing concentration of ISA in solution, a decrease of K_d can be observed, indicating that an interaction between Ca^{2+} and ISA takes place. The solid line in Fig. 2 is a best fit of the experimental data using Eq. (5) with $K_{ML} = K_{CaISA^+}$ and L = ISA. The experimental data can be described very well using a value of (19.3 $\pm$ 0.8) for K_{CaISA^+} ($I = 0.2\ M$). Extrapolating this value to zero ionic strength:

$$\log K^o_{CaISA^+} = \log K_{CaISA^+} - \log \gamma_{Ca} \qquad (11)$$

using the Davies' extension of the Debye-Hückel equation,[16] results in log $K^o_{CaISA^+} = (1.8 \pm 0.1)$.

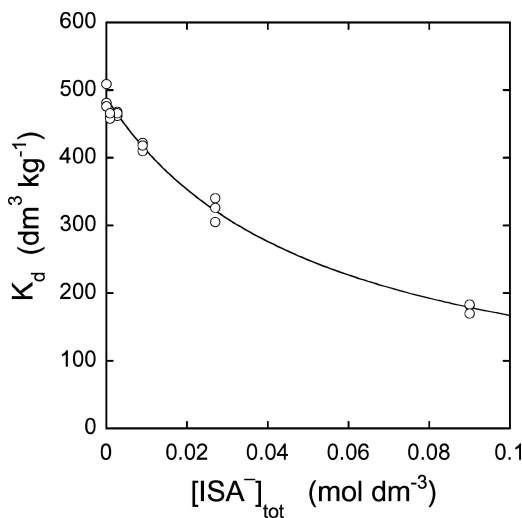**Fig. 2.** Dependence of the K_d of Ca as a function of the total concentration of α-isosaccharinate in the equilibrium solution ([ISA$^-$]$_{tot}$).

Table I. Overview of the Results of a Titration of a 10^{-4} M Ca solution with 0.88 M NaISA

NaISA (ml)	E (mV)	pH	$10^5[Ca]_{tot}$ (mol-dm^{-3})	$10^3[ISA^-]_{tot}$ (mol-dm^{-3})	I (mol-dm^{-3})	$10^5[Ca^{2+}]$ (mol-dm^{-3})	log K_{CaISA^+}	log $K^o_{CaISA^+}$
0.25	−45.7	6.22	9.90	8.63	0.207	8.70	1.21	1.72
0.50	−47.4	6.21	9.81	17.1	0.214	7.59	1.23	1.75
0.75	−48.8	5.95	9.71	25.4	0.220	6.78	1.23	1.75
1.00	−50.3	6.08	9.62	33.5	0.226	6.01	1.25	1.77
1.25	−51.4	6.12	9.53	41.5	0.233	5.50	1.25	1.77
1.50	−52.7	6.19	9.44	49.3	0.239	4.95	1.26	1.79
1.75	−53.7	6.00	9.35	57.0	0.245	4.57	1.26	1.79
2.00	−54.7	6.06	9.27	64.6	0.250	4.22	1.27	1.79
2.25	−55.8	6.12	9.18	72.0	0.256	3.86	1.28	1.81
2.50	−56.7	6.18	9.10	79.3	0.262	3.59	1.29	1.82

3.2. Measurements with CSE

Table I shows experimental data for the titration of a 10^{-4} M solution of Ca with ISA. Because the total Ca concentration is negligible compared to the ISA concentration, the ionic strength could be calculated simply based on the concentration of NaCl and the amount of added NaISA and considering the dilution caused by the addition of NaISA. Table I also shows the conditional K_{CaISA^+} values calculated for each titration point. The thermodynamic equilibrium constants valid for zero ionic strength, $K^o_{CaISA^+}$, were calculated according to Eq. (11). Owing to statistical and nonstatistical uncertainties, $K^o_{CaISA^+}$ is not perfectly constant throughout the titration. For this reason the optimal value for $K^o_{CaISA^+}$ has to be evaluated through an error minimization procedure. The difference between measured and calculated concentrations of free Ca^{2+} is used for that purpose. The optimal value for log $K^o_{CaISA^+}$ found in this way is 1.78, which is almost the same value as obtained by the average of the individual values given in Table I. Figure 3 shows the comparison between the measured Ca^{2+} concentrations and those calculated for log $K^o_{CaISA^+} = 1.78$. Note that each titration point has the same weight in the error minimization procedure. This is, in principle, not a good assumption, because the points at lower ISA concentrations have a larger uncertainty than those at higher ISA concentrations. The experimental uncertainty of E of ~0.2 mV has a much a larger impact on the calculation of $[Ca^{2+}]$ for the former data than for the latter. However, with respect to the $K^o_{CaISA^+}$ values determined at higher ISA concentrations, the optimal value for log $K^o_{CaISA^+}$ can, under any circumstances, exceed a value of 1.82. Since other error sources, such as uncertainties in volumetric additions, are negligible in comparison with the uncertainties in E and the optimization procedure, it is justified to specify the final result as log $K^o_{CaISA^+} = (1.78 \pm 0.04)$. A further reduction of the uncertainty
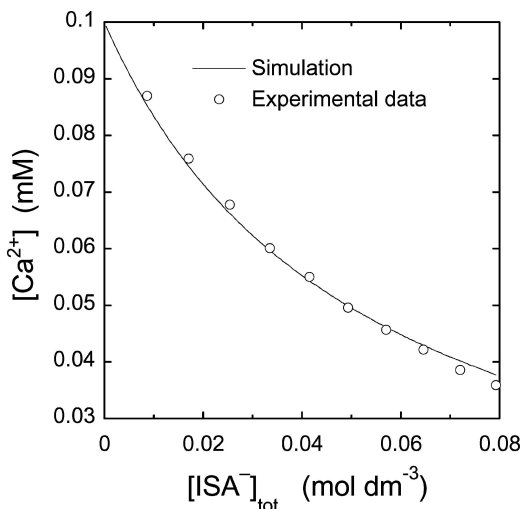
Fig. 3. Comparison between experimental data (*cf.*, Table I) obtained with the calcium-specific electrode and a simulation of the data using log $K^o_{CaISA^+}$ of 1.78. $[ISA^-]_{tot}$ is the total concentration of α-isosaccharinate in the equilibrium solution.

would be in principle possible, but in view of the already small number it is not worthwhile.

3.3. On the Solubility of Ca(α-ISA)$_{2(s)}$ in Aqueous Solutions

Table II shows a comparison of log $K^o_{CaISA^+}$ values obtained in the present work with values proposed in the literature that are relevant for calculating the solubility of Ca(ISA)$_{2(s)}$ at neutral pH. The log $K^o_{CaISA^+}$ value measured in the present work is in fair agreement with the value proposed by chemical analogy with other (poly)hydroxycarboxylic acids.[8] It is in slight disagreement with a value extracted from measurements of the solubility of Ca(ISA)$_{2(s)}$.[10] The latter value is, however, strongly correlated with the solubility product of Ca(ISA)$_{2(s)}$, because the effect of ion-pair formation on the solubility of Ca(ISA)$_{2(s)}$ is too weak to allow for an independent determination of $K^o_{CaISA^+}$ and K^o_{sol} to be made. In fact, predictions of the total Ca solution concentration will be similar for both of the data sets proposed by Rai *et al.*[10] and those by Vercammen *et al.*,[8] because the lower value of $K^o_{CaISA^+}$ proposed by Rai *et al.* is partly compensated by an accordingly larger value for the solubility product K^o_{sol}. Because the evaluation of $K^o_{CaISA^+}$ presented here is independent of the formation of Ca(ISA)$_{2(s)}$, and because it is in sufficient agreement with the value proposed in earlier work,[8,9] it

Table II. Overview of the Equilibrium Constants Relevant for Calculating the Solubility of $Ca(ISA)_{2(s)}$ at Neutral and Alkaline pH
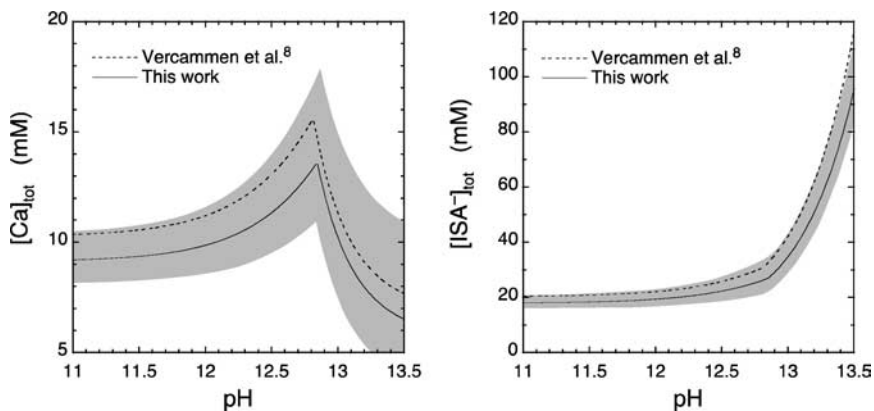
Equilibrium constant[a]	Value[a]	Reference
$\log K^{o}_{sol}$	$-(6.26 \pm 0.07)$	(10)
	$-(6.53 \pm 0.02)^{b}$	(9)
	$-(6.36 \pm 0.1)$	(8)
$\log K^{o}_{CaISA^{+}}$	(1.44 ± 0.07)	(10)
	1.70	(9)
	1.70	(8)
	(1.78 ± 0.04)	This study (by potentiometry)
	(1.80 ± 0.1)	This study (by ion exchange)
$\log K^{o}_{CaISA^{0}}$	$-(10.4 \pm 0.2)$	(8)

[a] Valid for zero ionic strength.
[b] In view of the new measurements of $K^{o}_{CaISA^{+}}$, it is proposed here to expand this uncertainty to ± 0.1.

is unnecessary to re-evaluate the solubility product, K^{o}_{sol}, measured in that work. A value of -6.53 for $\log K^{o}_{sol}$ is thus reasonable. However, in view of the new results for $K^{o}_{CaISA^{+}}$, it is proposed here that the uncertainty range of $\log K^{o}_{CaISA^{+}}$ is expanded to ± 0.1 logarithmic units (instead of ± 0.02). Note that K^{o}_{sol} evaluated from solubility measurements of $Ca(ISA)_{2(s)}$ at alkaline conditions[8] is thus in slight disagreement with this value. The measurements at alkaline pH have been, however, affected by kinetic precipitation phenomena and may be slightly less reliable than the measurements at neutral pH. Finally, it has to be noted that no indication of a 1:2 complex between Ca^{2+} and ISA^{-} has been found in the present work. Although the formation of such a complex has been postulated in previous work of Rai et al.,[17] recent measurements of Rai et al.[10] also gave no indication of such complexes being formed. From electrostatic considerations it is reasonable to assume that the interaction of a second ISA^{-} ligand with the monovalent $Ca(ISA)^{+}$ complex is much weaker than the interaction of ISA^{-} with the divalent Ca^{2+} ion, and that 1:2 complexes may only be formed at very large total ISA concentrations.

In view of the questions associated with the degradation of cellulose in a cementitious repository for radioactive waste and in order to assess the effects of the uncertainties involved in the thermodynamic constants on the solubility of $Ca(ISA)_{2(s)}$, the total solution concentrations of Ca and ISA are calculated at alkaline pH and compared to predictions made from earlier work. The thermodynamic data used for this purpose are on the one hand those of Vercammen et al.[8] (cf., Table II). On the other hand, the predictions made from the present work are based on $\log K^{o}_{CaISA^{+}} = (1.8 \pm 0.1)$, $\log K^{o}_{sol} = -(6.53 \pm 0.1)$ and $\log K^{o}_{CaISA^{+}} = -(10.4 \pm 0.2)$. Furthermore, the same values for the solubility product of $Ca(OH)_{2(s)}$ and the protolysis constant of water as in Vercammen

Fig. 4. Comparison between the predictions for total concentrations of Ca ($[Ca]_{tot}$) and α-isosaccharinate ($[ISA^-]_{tot}$) made by the equilibrium constants proposed in the present work (for the values used, the reader is referred to the text) and those of Vercammen *et al.*[8] Shaded areas are estimates of uncertainty introduced by the combined uncertainties of the equilibrium constants involved.

et al.[8] were used for both calculations. It is shown in Fig. 4 that the predictions made from the data of Vercammen *et al.*[8] are in agreement within the range of uncertainty with the dataset of the present work. Note that this range of uncertainty is based on a worst-case combination of the uncertainties specified for the equilibrium constants and not on a true propagation of these uncertainties. From all these considerations we abstain in the present work from reinterpreting the earlier data in the light of the new values proposed for $K^o_{CaISA^+}$.

4. CONCLUSIONS

The stability constant for the Ca(ISA)$^+$ ion pair was measured using two methods. In contrast to previous work, the present measurements were carried out in the absence of Ca(ISA)$_{2(s)}$. For this reason the results obtained are independent of the solubility product of Ca(ISA)$_{2(s)}$. Both methods give similar values for the equilibrium constant. The average value of the stability constant is log $K^o_{CaISA^+} = (1.8 \pm 0.1)$ for $I = 0$ and temperature $(22 \pm 1)°C$. This value is in reasonable agreement with the estimated value of $\log K^o_{CaISA^+} = 1.7$, which was used in previous studies[8,9] and is based on the analogy with the Ca-gluconate$^+$ ion pair.

The proposed formation of an ion pair, in which only the carboxylic group is involved, at neutral pH is in agreement with the generalized ionization-coordination theory developed by van Duin *et al.*[18] in 1989. At high pH values, however, the binding of Ca^{2+} with ISA$^-$ involves both a carboxylic group and a deprotonated α-OH group.[8]

ACKNOWLEDGMENTS

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