Solubility Products of Calcium Isosaccharinate and Calcium Gluconate

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The solubility products of the calcium salts of two polyhydroxy ligands (PHL), isosaccharinate (ISA) and gluconate (GLUC), were measured. Solubility products of $\log K_{s,o} = -6.22 \pm 0.03$ at $I = 0$ and $T = 20 \pm 1$ °C for Ca(α-ISA)$_2$, and $\log K_{s,o} = -3.54 \pm 0.06$ at $I = 0$ and $T = 20 \pm 1$ °C for Ca(GLUC)$_2$ were calculated ignoring the complexation equilibrium: Ca^{2+} + PHL$^-$ $\rightleftharpoons$ CaPHL$^+$. If this complexation reaction is taken into account with $\log K_1^{\circ} = 1.7$, the values of the solubility products are $\log K_{s,o} = -6.53 \pm 0.02$ at $I = 0$ for Ca(α-ISA)$_2$ and $\log K_{s,o} = -4.19 \pm 0.05$ at $I = 0$ for Ca(GLUC)$_2$. Both dissolution reactions are endothermic. The standard free enthalpy change (ΔH°) for Ca(α-ISA)$_2$ is 40 ± 1 kJ mol^{-1} and 37 ± 4 kJ mol^{-1} for Ca(GLUC)$_2$. The enthalpy was assumed to be constant in the temperature range $7 < T < 90$ °C. The calculated standard entropy change (ΔS°) is 17 ± 5 J mol^{-1} K^{-1} for Ca(α-ISA)$_2$ and 60 ± 14 J mol^{-1} K^{-1} for Ca(GLUC)$_2$.

In Switzerland short-lived low- and intermediate-level radioactive waste (L/ILW) is planned to be emplaced in a deep underground repository.[1] The use of large amounts of cement in constructing this repository creates an alkaline environment in which the pH of the pore solutions remains above 12.5 for times of the order of 10^5 years. Generally this ensures the strong sorption of most radionuclides on the cement phases and a consequently slow release to the geo- and biosphere.[2] However, the presence of organics in the waste and the formation of aqueous radionuclide–organic complexes can decrease the sorption of radionuclides and enhance their release from the repository. The extent to which organic ligands might effect sorption depends strongly on their concentration in the cement pore water.[3]

One way in which organic ligand concentrations may be limited is the formation of sparingly soluble salts with Ca^{2+}. For example, it was shown in some earlier work[4] that the concentration of oxalate in a fresh cement pore water could not be higher than 10^{-5} M due to the formation of sparingly soluble Ca-oxalate solids (whewellite and weddelite). With respect to repository safety, the formation of such sparingly soluble salts is advantageous, especially for ligands such as gluconic acid[5] and isosaccharinic acid,[6] with a strong affinity towards tri- and tetravalent radionuclides. Both gluconic and isosaccharinic acid (Fig. 1) belong to the class of polyhydroxy ligands (PHL). Gluconic acid (GLUC) is a cement
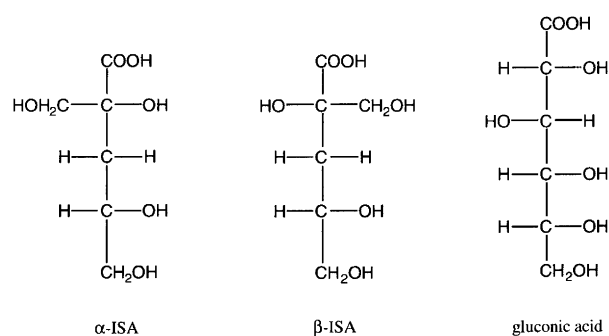
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Fig. 1. Molecular structure of gluconic acid and α/β-isosaccharinic acid.

additive used to improve the workability of cement. Although solubility studies for Ca(GLUC)$_2$ have been performed,[7,8] the solubility product is still unknown. Isosaccharinic acid (ISA) is the main degradation product of the alkaline degradation of cellulose,[9,10] a substantial waste component.[2] Two diastereomers of ISA are formed during the alkaline degradation of cellulose: α- and β-ISA (Fig. 1). α-ISA forms 'sparingly soluble' Ca salts,[11] whereas β-ISA forms 'highly soluble' Ca salts.[12]

In cement pore water, the concentration of Ca^{2+} is buffered owing to the dissolution of Ca(OH)$_2$ (portlandite). If the stoichiometric equivalent of Ca(OH)$_2$ present in the cement largely exceeds the stoichiometric equivalent of the ISA or the gluconate present in the pore water, the formation of solid Ca(α/β-ISA)$_2$ and/or Ca(GLUC)$_2$ (and consequently also the concentration

of free α/β-ISA and GLUC) will be governed by the dissolution equilibrium of portlandite.

The solubility products of Ca(α-ISA)$_2$, Ca(β-ISA)$_2$ and Ca(GLUC)$_2$, however, are not known, and therefore it is not possible to calculate the maximum concentration of these ligands in solution. In this study we measured the solubility product of Ca(α-ISA)$_2$ and Ca(GLUC)$_2$. Further, we measured the temperature dependency of the solubility of Ca(α-ISA)$_2$ and derived the standard free enthalpy for the dissolution reaction. Similar calculations were made for Ca(GLUC)$_2$ based on literature data.[7,8]

Material and methods

Synthesis of Ca(α-ISA)$_2$. Ca(α-ISA)$_2$ was prepared by treating lactose with saturated limewater as decribed by Whistler and BeMiller.[11]

Solubility of Ca(α-ISA)$_2$ and Ca(GLUC)$_2$ at constant temperature.

Ca(α-ISA)$_2$. About 150 mg of Ca(α-ISA)$_2$, 10 g of demineralised water and varying amounts of a cation exchange resin in the Na$^+$ form (Chelex-100, Biorad) between 0.25 and 3 g (Table 2) were mixed in a centrifuge tube (polysulfonate, Nalgene) and shaken end-over-end for 24 h at $20 \pm 1\,°C$. By using a cation-exchange resin (in the Na$^+$ form), the concentrations of Na$^+$, Ca^{2+} and α-ISA$^-$ could be changed simultaneously without the addition of extra chemicals. The resin and the remaining Ca(α-ISA)$_2$ were filtered off by a membrane filter (0.45 μm, Acrodisc, Gelman), and the solutions were analysed for Na and Ca by ICP-AES and for α-ISA by ion chromatography (Dionex 2010i, HPIC-AS4A column, Na$_2$CO$_3$/NaHCO$_3$ eluent at a flow rate of 1 ml min^{-1}, suppressed conductivity detection mode). The relative standard uncertainty on the measurements was $\pm 2\%$ for Na, $\pm 5\%$ for Ca and $\pm 5\%$ for α-ISA. No difference was found (data not shown) between centrifuging the samples (27 000 g, 30 min) and filtrating the

samples, indicating that colloids were not formed in significant amounts.

Ca(GLUC)$_2$. The same procedure was used for the solubility studies of Ca-gluconate. Because of the higher solubility of Ca(GLUC)$_2$, about 1 g of Ca(GLUC)$_2$ was used (Ca(GLUC)$_2 \cdot H_2O$, Merck). The amounts of demineralised water and resin (Table 1) were similar to those used in the Ca(α-ISA)$_2$ solubility study. Gluconate in solution was measured by HPLC (Dionex DX 500, Carbopac PA100 column, 0.1 M NaOH/0.1 M Na-acetate eluent at a flow rate of 1 ml min^{-1}, pulsed amperometric detection mode). The relative standard uncertainty on the GLUC measurement was $\pm 5\%$.

Solubility of Ca(α-ISA)$_2$ at varying temperature. About 300 mg of Ca(α-ISA)$_2$ were mixed with 20 ml demineralised water in 50 ml centrifuge tubes (polysulfonate, Nalgene). The mixtures were equilibrated for 24 h in a temperature-controlled shaking equipment. This time was found to be sufficient to reach dissolution equilibrium. The temperature was varied between 2 and 50 °C. The samples were filtered through a membrane filter (0.45 μm, Acrodisc, Gelman). The filtrates were diluted 100 times and 10 times for ISA analysis and Ca analysis, respectively. α-ISA was measured by HPLC (Dionex DX-500, 80 mM NaOH eluent at a flow rate of 1 ml min^{-1}, suppressed conductivity detection mode) and Ca by ICP-AES. The reason for using a different method for analysing α-ISA in these tests was that the Dionex 2010i system was replaced by a Dionex DX-500 system. The relative standard uncertainty on the ISA measurement was $\pm 5\%$.

Results and discussion

Table 1 gives an overview of the composition of the solutions in equilibrium with Ca(GLUC)$_2$ and the Chelex-100 resin. Table 2 gives the corresponding results for Ca(α-ISA)$_2$. With an increasing amount of ion-exchange resin, the concentration of calcium in solution

Table 1. Reaction conditions and analytical results for the gluconate solutions in equilibrium with an ion-exchange resin.[a]

Ca(GLUC)$_2 \cdot H_2O$/ g	Resin/ g	Water/ g	[Na]/ mM	[Ca]/ mM	[GLUC]/ mM	log a_{Ca}	log a_{GLUC}	log $K_{s,o}$
1.01	0	10.00	<0.04	75.6±3.8	154±8	−1.63 (−2.02)	−0.94 (−1.08)	−3.51 (−4.19)
1.02	0.234	10.17	13.0±0.3	68.1±3.4	145±7	−1.67 (−2.06)	−0.96 (−1.09)	−3.60 (−4.25)
1.01	0.540	10.40	28.5±0.6	62.9±3.1	151±8	−1.71 (−2.12)	−0.95 (−1.06)	−3.60 (−4.25)
1.06	0.888	10.66	44.8±0.9	56.1±2.8	155±8	−1.75 (−2.19)	−0.94 (−1.03)	−3.63 (−4.26)
1.02	1.173	10.87	58.3±1.2	52.4±2.6	166±8	−1.79 (−2.25)	−0.91 (−0.98)	−3.60 (−4.23)
1.02	1.306	10.97	66.6±1.3	55.1±2.8	176±9	−1.77(−2.25)	−0.88 (−0.96)	−3.53 (−4.18)
0.96	1.591	11.18	77.4±1.5	51.4±2.6	178±9	−1.80 (−2.29)	−0.88 (−0.95)	−3.55 (−4.20)
0.98	1.779	11.32	82.7±1.7	50.2±2.5	189±9	−1.81 (−2.32)	−0.85 (−0.92)	−3.51 (−4.17)
0.98	2.241	11.66	100.1±2.0	48.4±2.4	205±10	−1.83 (−2.37)	−0.82 (−0.87)	−3.47 (−4.13)
1.01	2.982	12.21	122.7±2.5	43.2±2.2	214±11	−1.88 (−2.44)	−0.80 (−0.84)	−3.48 (−4.14)
0.98	3.989	12.95	146.6±3.0	38.7±1.9	236±12	−1.93 (−2.54)	−0.76 (−0.79)	−3.45 (−4.12)

[a] Values in parenthesis represent the values of the corresponding parameter calculated by taking the complexation equilibrium according to eqn. (5) into account. The pH of the solutions was between 6.5 and 8. $T = 20 \pm 1\,°C$.

Table 2. Reaction conditions and analytical results for the ISA solutions in equilibrium with an ion-exchange resin.[a]

Ca(α-ISA)₂/ g	Resin/ g	Water/ g	[Na]/ nM	[Ca]/ mM	[α-ISA]/ mM	log a_{Ca}	log a_{ISA}	log $K_{s,o}$
0.158	0.251	10.41	12.0±0.2	3.62±0.18	18.4±0.9	−2.69 (−2.85)	−1.78 (−1.82)	−6.25 (−6.50)
0.157	0.509	10.40	23.1±0.5	1.97±0.09	27.5±1.4	−2.98 (−3.21)	−1.64 (−1.63)	−6.26 (−6.49)
0.161	0.749	10.68	30.1±0.6	1.45±0.07	32.7±1.6	−3.13 (−3.39)	−1.55 (−1.56)	−6.23 (−6.51)
0.159	1.041	10.94	38.3±0.7	1.09±0.05	40.1±2.0	−3.28 (−3.56)	−1.47 (−1.47)	−6.22 (−6.52)
0.161	1.275	11.12	43.9±0.8	0.91±0.05	44.0±2.2	−3.37 (−3.67)	−1.42 (−1.43)	−6.21 (−6.55)
0.159	1.596	11.51	49.6±0.9	0.79±0.04	50.3±2.5	−3.44 (−3.77)	−1.38 (−1.38)	−6.19 (−6.54)
0.157	1.746	11.46	51.8±1.0	0.73±0.04	52.3±2.6	−3.48 (−3.81)	−1.36 (−1.36)	−6.20 (−6.55)
0.161	2.011	11.60	55.7±1.1	0.68±0.03	58.0±2.9	−3.52 (−3.87)	−1.33 (−1.32)	−6.18 (−6.53)
0.161	3.088	12.44	65.7±1.3	0.53±0.03	67.6±3.4	−3.64 (−4.03)	−1.27 (−1.26)	−6.18 (−6.55)

[a]Values in parenthesis represent the values of the corresponding parameter calculated by taking the complexation equilibrium according to eqn. (5) into account. The pH of the solutions was between 6.5 and 8. $T = 20 \pm 1\,°C$.

decreases and the concentration of sodium and α-ISA or GLUC, increases. Ca^{2+} in solution adsorbs on the resin and displaces Na^+. The decrease of Ca^{2+} in solution causes dissolution of $Ca(α\text{-}ISA)_2$ or $Ca(GLUC)_2$ until the solubility equilibria have been re-established.

The dissolution equilibrium of a sparingly soluble $Ca(PHL)_2$ solid can be written as

$$Ca(PHL)_2 \rightleftharpoons Ca^{2+} + 2\,PHL^- \tag{1}$$

The solubility product, $K_{s,o}$, is defined as

$$K_{s,o} = a_{Ca^{2+}}(a_{PHL^-})^2 \tag{2}$$

where $a_{Ca^{2+}}$ is the activity of Ca^{2+} in solution and a_{PHL^-} is the activity of PHL^- in solution.

In a first step, it is assumed that this is the only relevant reaction. The activities of Ca^{2+} and PHL^- are calculated from the analytical concentration of Ca and PHL (=GLUC or α-ISA) in solution and the activity coefficients $γ_i$. The activity coefficients are calculated using the 'Davies' extension of the Debye–Hückel equation[13] given by:

$$\log γ_i = -Az_i^2[I^{1/2}/(1 + I^{1/2}) - 0.3I] \tag{3}$$

where I is the ionic strength of the solution, z_i the charge of the ion i and A a constant defined by

$$A = \frac{1.82 \times 10^6}{(εT)^{3/2}} \tag{4}$$

where ε is the dielectric constant of water (depending on temperature) and T is the absolute temperature (in K).

Gluconate is known to form weak complexes (ion pair formation) with Ca^{2+} under neutral conditions according to[14]

$$Ca^{2+} + PHL^- \rightleftharpoons CaPHL^+ \tag{5}$$

with a stability constant $\log K_1^\circ = 1.7$. For calculating the solubility product, this side reaction should be taken into account. The activity of the free Ca^{2+} and $GLUC^-$ will now be smaller than can be calculated from the total concentration of Ca and gluconate. Table 1 shows the values of the activities of Ca and GLUC, and the resulting solubility product of $Ca(GLUC)_2$ calculated

from eqn. (2). Two sets of values for $\log K_{s,o}$ are given: one set takes into account the weak complexation between Ca^{2+} and $GLUC^-$, in the other set this is ignored. All calculations were performed with the geochemical speciation program PHREEQE.[15] The average value of $\log K_{s,o}$ for $Ca(GLUC)_2$ is -4.19 ± 0.05 at $T = 20 \pm 1\,°C$ when complexation reaction (5) is taken into account, and -3.54 ± 0.06 when complexation is ignored. De Carli[7] measured the solubility of $Ca(GLUC)_2$ in water as a function of temperature. For a temperature of 20 °C, he measured a solubility of 36 g L⁻¹. From these data [based on reaction (1) with $PHL^- = GLUC^-$] we calculated a solubility product $\log K_{s,o} = -3.41$, ignoring complexation equilibrium (5). This value is in good agreement with the value reported in this study.

The solubility product for $Ca(α\text{-}ISA)_2$ was calculated in a similar way. Because no information exists on the formation of complexes between Ca^{2+} and $α\text{-}ISA^-$, it was assumed that, to a first approximation, a similar complex was formed according to eqn. (5) with the same stability constant as for $Ca(GLUC)^+$, i.e. $\log K_1^\circ = 1.7$. This assumption was based on the fact that ligands with a similar structure generally form, with a given metal, complexes of similar stability. Table 3 gives an overview of some (poly)hydroxycarboxylic acids and their corresponding equilibrium constants for the formation of a positively charged $Ca(PHL)^+$ complex according to eqn. (5). The results of the calculations for ISA, carried out in a similar manner to these described for GLUC, have been summarised in Table 2. The average value for $\log K_{s,o}$ is -6.22 ± 0.03 at $T = 20 \pm 1\,°C$ when complexation is ignored and -6.53 ± 0.02 when complexation is taken into account. The results are in fairly good accord with measurements performed by Alén,[22] who measured a solubility of $Ca(α\text{-}ISA)_2$ of 2.4 g L⁻¹ at 21 °C. The corresponding solubility product calculated from this measurement is $\log K_{s,o} = -6.45$, ignoring the complexation equilibrium.

Table 4 gives an overview of the composition of the solutions in equilibrium with solid $Ca(α\text{-}ISA)_2$ at different temperatures. The concentration of Ca and ISA increases with increasing temperature. Hence the solubil-

Table 3. (Poly)hydroxycarboxylic acids and their correspond-
ing equilibrium constants for the formation of a positive
Ca(PHL)$^+$ complex (I = 0 M, T = 25 °C).

Ligand	Structure	log K_1°	Ref.
Glycollic acid	HO·CH$_2$·COOH	1.59	17
		1.62[a]	18[b]
		1.65	19
Lactic acid	CH$_3$·CH(OH)·COOH	1.46[a]	20
		1.47	17
		1.55	21
		1.42	16
		1.57[a]	18[b]
Glyceric acid	HO·CH$_2$·CH(OH)·COOH	1.69[a]	18[b]
Gluconic acid	HO·CH$_2$·(CHOH)$_4$·COOH	1.59[a]	20
		1.70	14
		1.72[a]	18[b]

[a]Values corrected for I = 0 using the Davies relation, eqn. (3).
[b]Temperature not specified.

Table 4. Dependence of the composition of aqueous solu-
tions in equilibrium with solid Ca(α-ISA)$_2$ on temperature.

T °C	α-ISA/ mM	Ca/ mM	$K_{s,o}$	log $K_{s,o}$
2.6	6.3 ± 0.6	3.5 ± 0.1	(8.0 ± 0.8) × 10^{-8}	−7.10
7.8	8.8 ± 0.3	4.4 ± 0.1	(1.7 ± 0.1) × 10^{-7}	−6.77
10	10.9 ± 0.1	5.4 ± 0.1	(3.1 ± 0.1) × 10^{-7}	−6.51
12.7	10.8 ± 0.1	5.3 ± 0.1	(2.9 ± 0.1) × 10^{-7}	−6.54
15.7	12.3 ± 0.1	6.6 ± 0.1	(4.5 ± 0.1) × 10^{-7}	−6.35
20.3	13.8 ± 0.2	7.6 ± 0.1	(6.2 ± 0.2) × 10^{-7}	−6.21
25.8	14.5 ± 0.9	8.2 ± 0.3	(7.1 ± 0.9) × 10^{-7}	−6.15
30.4	17.4 ± 0.1	9.0 ± 0.1	(1.1 ± 0.1) × 10^{-6}	−5.96
36	19.4 ± 0.2	9.9 ± 0.1	(1.4 ± 0.1) × 10^{-6}	−5.85
42	21.3 ± 0.2	10.9 ± 0.1	(1.7 ± 0.1) × 10^{-6}	−5.77
50.4	23.8 ± 0.1	12.3 ± 0.1	(2.3 ± 0.1) × 10^{-6}	−5.64

ity of Ca(α-ISA)$_2$ increases with temperature, indicating
that we are dealing with an endothermic process. The
concentration of α-ISA is twice the concentration of Ca,
which is consistent with reaction (1). The solubility
product was calculated by applying eqn. (2). Activity
coefficients were calculated using eqn. (3). The com-
plexation reaction (5) was ignored because the temper-
ature dependency of this reaction is not known. The
standard reaction enthalpy (ΔH°) can be calculated from
the temperature dependency of $K_{s,o}$ at constant pressure:

$$\frac{d \ln K_{s,o}}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{6}$$

which is known as the van't Hoff equation. Under the
assumption that ΔH° is independent of temperature and
that the heat capacity of the reaction, ΔC_p°, is close to
zero,[23] eqn. (6) can be simply integrated to yield

$$\ln K_{s,o} = -\frac{\Delta H^\circ}{RT} + C \tag{7}$$

where C is an integration constant. A plot of log $K_{s,o}$
against the reciprocal absolute temperature yields a

straight line with slope $0.434\Delta H^\circ/R$. Figure 2 shows a
plot of log $K_{s,o}$ as a funtion of the reciprocal temperature.
The data-set for Ca(α-ISA)$_2$ contains data from this
work and unpublished data from Alén.[22] The two sets
are in good accord. The plot shown in Fig. 2 is a linear
one, indicating that the above assumptions (ΔH° is
independent of temperature, the heat capacity of the
reaction, ΔC_p°, is close to zero) are justified for the
solubility of Ca(α-ISA)$_2$ in the temperature range
$7 < T < 90$ °C. The standard reaction enthalpy for reac-
tion (1) was calculated from the slope of the linear fit
and is 40 ± 1 kJ mol^{-1}. With this standard reaction
enthalpy, the solubility product at a given temperature,
T_1, can be recalculated for a temperature T_2 by

$$\ln \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \tag{8}$$

De Carli[7] and May et al.[8] published data on the solubility
of Ca(GLUC)$_2$ at different temperatures. These values
are given in Table 5, together with calculated solubility
products [ignoring reaction (5)]. Only the solubility data
up to 40 °C were used, because at higher temperatures,
the solubility was so high that the ionic strength of the
solutions becomes larger than 0.5 M and eqn. (3) could
no longer be used for activity coefficient calculations.
The increasing solubility at increasing temperature indi-
cates that the solubilisation of Ca(GLUC)$_2$ is also an
endothermic process. From the plot of log $K_{s,o}$ against
the reciprocal temperature (Fig. 2), a value of $\Delta H^\circ =$
37 ± 4 kJ mol^{-1} was calculated. This value is similar to
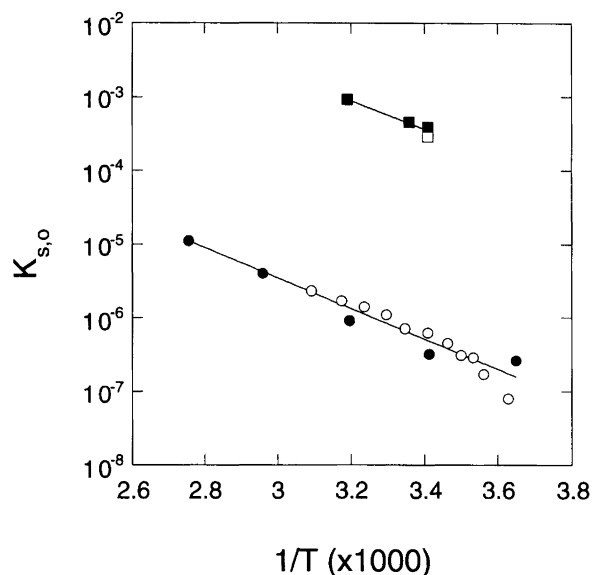the one calculated for Ca(α-ISA)$_2$.

Fig. 2. Plot of the solubility product of Ca(α-ISA)$_2$ (circles:
filled symbols represent unpublished data of Alén;[22] open
symbols are data of this study) and Ca(GLUC)$_2$ (squares:
filled symbols represent data from De Carli[7] and May et al.;[8]
open symbols represent data from this study) as a function
of the reciprocal temperature. The uncertainty in the ISA
data of this work is given in Table 4.

Table 5. Dependence of the solubility of Ca(GLUC)$_2$ on temperature (data from De Carli,[7] May *et al.*[8]).

Temperature/°C	Ca(GLUC)$_2$/g L^{-1}	[Ca]/mM	[GLUC]/mM	I/M	log $K_{s,o}$
20	36.0	84	167	0.25	−3.41
25[a]	38.5[a]	90[a]	179[a]	0.27[a]	−3.34[a]
40	50.2	117	234	0.35	−3.04
60.2	108	251	502	0.75	N.C.[b]
69	132	307	613	0.92	N.C.[b]
90	269	626	1251	1.88	N.C.[b]
96.4	364	847	1693	2.54	N.C.[b]

[a]Data from May *et al.*[8] [b]N.C., not calculated.

From the solubility products, the standard Gibbs free energy change ($\Delta G°$) for reaction (1) can be calculated

$$\Delta G° = -RT \ln K_{s,o} \qquad (9)$$

For Ca(α-ISA)$_2$, $\Delta G°$ is 35 ± 1 kJ mol^{-1} at 25 °C. The value calculated for Ca(GLUC)$_2$ is 19 ± 1 kJ mol^{-1} at 25 °C. The standard reaction entropy ($\Delta S°$) is given by the following relationship

$$\Delta G° = \Delta H° - T\Delta S° \qquad (10)$$

The standard reaction entropies for the dissolution of Ca(α-ISA)$_2$ and Ca(GLUC)$_2$ are 17 ± 5 and 60 ± 14 J mol^{-1} K^{-1}, respectively.

Applications

With the solubility data measured, it is possible to estimate the maximum concentration of α-ISA and gluconate that might be expected in a cement pore water. In the early degradation stage of the cement, dissolution of Na–K–OH determines the pH of the cement pore water.[24] The pH of the pore water at this stage is 13.3, and the concentration of Ca in such water is ca. 2 mM. In the second stage of cement degradation, dissolution of Ca(OH)$_2$ determines the water chemistry of the cement pore water. At this stage of cement degradation, the Ca concentration in the pore water equals ca. 20 mM. A rough estimation of the maximum concentration of α-ISA and GLUC can be made using eqn. (2):

$$K_s = [Ca^{2+}][PHL]^2 \qquad (11)$$

$$[PHL] = (K_s/[Ca^{2+}])^{1/2} \qquad (12)$$

where K_s is the conditional solubility product and [PHL] the concentration of the polyhydroxy ligand (α-ISA or GLUC). As the stability constant of the Ca–ISA complex is not known, the Ca complexation equilibria were neglected, and the solubility products derived by ignoring Ca complexation equilibria were taken: log $K_{s,o} = -3.54 \pm 0.06$ for Ca(GLUC)$_2$ and log $K_{s,o} = -6.22 \pm 0.03$ for Ca(α-ISA)$_2$. The conditional solubility products, K_s, were calculated from the thermodynamic constants, $K_{s,o}$:

$$K_s = K_{s,o}/(\gamma_{Ca^{2+}}\gamma_{PHL^-}) \qquad (13)$$

using the Davies equation for γ_i. The concentration of

Ca^{2+} in the pore water is fixed by the saturation equilibrium of portlandite at the given pH. Table 6 shows the calculated maximum concentrations of α-ISA and GLUC in equilibrium with Ca^{2+} for two stages of cement degradation. The calculations show that the solubility limits of Ca(α-ISA)$_2$ and Ca(GLUC)$_2$ result in relatively high concentrations of α-ISA and GLUC in cement pore water. According to Wieland *et al.*[25] concentrations of α-ISA of ca. 0.01 M result in sorption reduction factors of 10^4–10^5 for Th^{IV}, often taken as a chemical analogue for tetravalent actinides. As gluconate forms stronger complexes than ISA, similar reduction factors will be reached at gluconate concentrations even lower than 10^{-2} M. These 'back-of-the-envelope calculations' demonstrate that the formation of Ca solids (in the case of gluconate and ISA) does not limit the effect of these ligands on radionuclide sorption to a negligible one. As shown elsewhere,[3,26,27] the sorption of ISA and GLUC on cement phases is a much more effective process in reducing the concentration of PHL in the pore water and consequently in limiting their effect on radionuclide sorption.

Conclusions

The dissolutions of Ca(α-ISA)$_2$ and Ca(GLUC)$_2$ are endothermic reactions ($\Delta H° > 0$). The increase in solubility with temperature is roughly the same for both reactions, reflected in similar values for $\Delta H°$. The larger solubility of Ca(GLUC)$_2$ as compared with Ca(α-ISA)$_2$ can be explained by a larger increase in entropy ($\Delta S°$) for Ca(GLUC)$_2$. An overview of all the thermodynamic data at 25 °C is given in Table 7. The difference in entropy cannot be explained as yet at a molecular level. The crystal structure of Ca(GLUC)$_2$ might be more ordered,

Table 6. Calculated maximum concentrations of α-ISA and GLUC in the cement pore water for different stages of cement degradation.

Stage	pH	[Ca]/ mM	I^a/ M	[α-ISA]$_{max}$^{b}/ mM	[GLUC]$_{max}$^{b}/ mM
I	13.3	2	0.3	44	930
II	12.5	20	0.05	10	220

[a]I, ionic strength. [b]Calculated by eqn. (12).

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Table 7. Overview of thermodynamic data for the dissolution of Ca(α-ISA)$_2$ and Ca(GLUC)$_2$ in water at 25 °C.

Solid phase	log $K_{s,o}$[a]	$\Delta G°$/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/ kJ mol^{-1} K^{-1}
Ca(GLUC)$_2$	−3.33	19±1	37±4	0.060±0.014
Ca(α-ISA)$_2$	−6.14	35±1	40±1	0.017±0.005

[a] Ignoring eqn. (5).

resulting in a larger increase in disorder when it goes into solution.

The formation of Ca solids of ISA and GLUC is not a significant factor in reducing the effects of these ligands on radionuclide sorption in the near field.

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