Interaction of Calcium with Sugar Type Ligands in Solutions Related to the Bayer Process

PhD. Theses

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1. Introduction

The gluconate (hereafter $Gluc^-$) is known to form complexes in solution with various metal ions. Complex solution species of $Gluc^-$ with Ca^{2+} and Al^{3+} (the two metal ions of importance in the current work) are reasonably well established. It is well known that Ca^{2+} forms weak $Gluc^-$ complexes of 1:1 composition in the usual ($2 < pH < 12$) range. Complexes with Al^{3+} and $Gluc^-$ in the same pH range are also well established.

Relatively little is known about the complexes forming in strongly alkaline solutions (those relevant to the Bayer process) in $Ca^{2+}/Gluc^-$, $Al^{3+}/Gluc^-$ binary and $Ca^{2+}/Al^{3+}/Gluc^-$ ternary systems.

We found that Ca^{2+} ion forms stable complexes with $Gluc^-$ in pure, aqueous NaOH solutions. The formation of $Ca^{2+} - Gluc^-$ complexes significantly enhances the solubility of calcium at high pH (relative to analogous pure NaOH solutions), and the stability constants are high enough to prevent the precipitation of $Ca(OH)_2$ in systems with $pH > 13$ and $[Gluc^-]_T > [Ca^{2+}]_T$. These high-pH complexes are formed *via* binding the calcium ion to the (deprotonated) alcoholate moiety on the C2 and/or C3 positions of gluconate, forming bonding isomers. At $pH \geq 12$ the predominant solution species formed are polynuclear in nature.

The $Al(OH)_4^-$ was also found to form stable complex with gluconate in alkaline solutions. The formation of this complex does not involve binding or release of hydroxide ions; most probably condensation takes place with the release of water.

Potentiometric titration curves obtained for the $Ca^{2+}/Al(OH)_4^-/Gluc^-$ ternary systems are markedly different from the sum of those found for the binary systems indicating the formation of complexes comprising of these three components (*i.e.,* ternary complexes). In these systems intense proton exchange is observed, which is a sign that the ternary complex is of extremely high stability.

2. Experimental

All materials [calcium chloride (CaCl$_2$, Molar Chemicals, puriss), hydrogen chloride (HCl), sodium hydroxide (NaOH, VWR, a.r grade), sodium gluconate (NaGluc, Sigma-Aldrich, ≥ 99 %), sodium heptagluconate (NaHglu, Sigma-Aldrich), glucose (Gls, Sigma-Aldrich, ACS reagent), calcium heptagluconate (CaHglu$_2$, Sigma-Aldrich, ≥ 98.0 %), sorbitol (Sigma-Aldrich, ≥ 98 %), arabic acid (HAra, Sigma-Aldrich), mucic acid (H$_2$Muc, Sigma-Aldrich, ≥ 97 %), aluminium wire (J. M. & Co, 99.99 %)] used for experiments were used as received without any further purification. The preparation of the carbonate-free sodium hydroxide solutions and of the Al(OH)$_4^-$ solutions were performed according to well-established procedures.

The NMR analysis of the samples were carried out using a BRUKER Avance DRX 500 NMR spectrometer equipped with a 5 mm inverse broadband probe-head furnished with z oriented magnetic field gradient capability. Experimental protocol was also built to record ^{43}Ca or ^{27}Al NMR spectra, respectively.

Potentiometric titrations were performed with the Metrohm 888 Titrando package using home-made platinised-platinum hydrogen (H$_2$/Pt) indicator electrode and Ag/AgCl reference electrode.

Molecular modelling was performed using Hartree−Fock *ab initio* calculations applying the 6-31G** basis set included in the Hyperchem program package. The Ca K-edge X-ray absorption spectra spectra were recorded in the Advanced Photon Source (APS) of Argonne National Laboratory (Argonne, IL USA).

The used solubility apparatus was designed, constructed and validated by us. Determination of the Ca^{2+} concentration in the supernatant was done using a Thermo's IRIS Intrepid II ICP-OES spectrometer and the solid phase was analyzed by powder X-ray diffraction (XRD) patterns registered on a Philips PW1710 instrument. The morphologies of the substances obtained were studied using a Hitachi S-4700 scanning electron microscope (SEM) and the relative quantities of the ions in the solid samples were determined with a Röntec QX2 energy dispersive X-ray fluorescence (EDX) spectrometer coupled to the microscope.

3. New results

3.1. Binary systems containing gluconate (Gluc⁻)

At pH < 11 the Ca^{2+} ion interacts with the OH group on C2 or C3 of the Gluc⁻, and two isomers of the $CaGluc^+$ complex are formed in aqueous solution having five- and six-membered chelate structures and they are in equilibrium.

Investigation of the $H^+/Gluc^-$ system showed that NMR spectroscopy was suitable to derive precise stability constants (log K_a= 3.23 ± 0.01), accordingly the $Ca^{2+}/Gluc^-$ system has been studied analogously. From the ionic strength dependence of its formation constant, the stability constant at $6 \leq pH \leq 11$ and at $I \rightarrow 0$ M has been derived (log $K^0_{1,1}$ = 1.5 ± 0.4).

The identification of the binding sites was experimentally approached *via* two-dimensional $^1H–^{43}Ca$ NMR measurements (*Figure 1*).

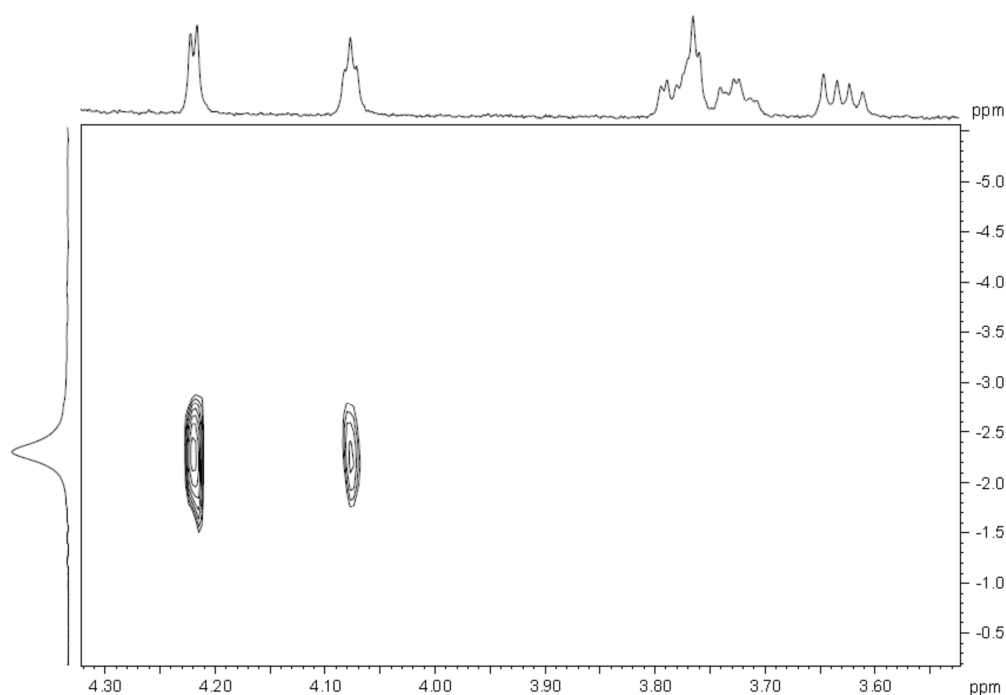*Figure 1: The two dimensional $^1H – ^{43}Ca$ NMR spectrum of the system containing Ca^{2+} and Gluc⁻ system at pH ~7*
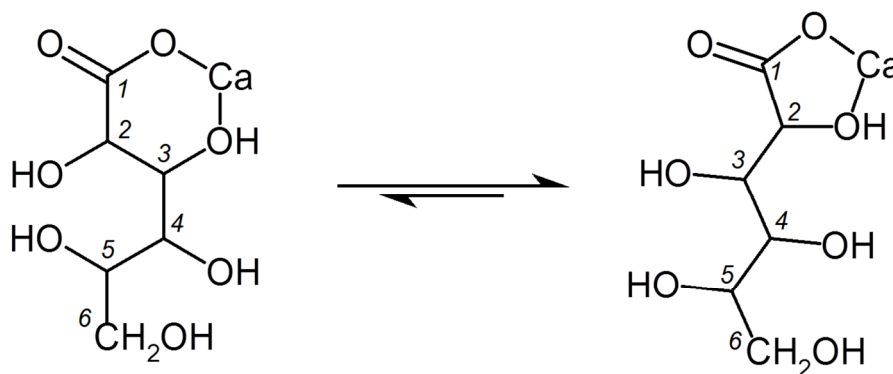
Figure 2: The suggested structures for the two bonding isomers of the CaGluc$^+$ complex forming in aqueous solution

Molecular modelling calculations resulted in multidentate bonding isomers with Ca^{2+} in bonding interactions with O(C1), O(C2), O(C3) and O(C6) (five-membered chelate, and a macrochelate reminiscent to scorpionate type compounds), or with O(C1), O(C3) and O(C5) (six-membered chelate).

3.2. Binary systems containing other sugar derivatives

Scorpionate type complexes with Ca^{2+} are formed not only with Gluc$^-$, but also with other simple sugar type ligands (*e.g.*, Hglu$^-$) in aqueous solutions, creating a novel class of scorpionate complexes.

In order to study the role of various functional groups in carbohydrate derivatives in complexing to Ca^{2+} ion, a range of sugar derivatives structurally related to Gluc$^-$ has been selected for further study. The selection criteria were on one hand altering the oxidation states of the terminal groups and keeping the chain length of the Gluc$^-$, and on the other hand keeping the oxidation states of the terminal group but increasing or decreasing the chain length. Investigations of the systems containing glucose (Glu), sorbitol (Sor), mucinate (Muc^{2-}), heptagluconate (Hglu$^-$) or arabinate (Ara$^-$) have been performed. The techniques used were multinuclear NMR spectroscopy, potentiometric titration, XAS measurements and molecular modelling calculations.
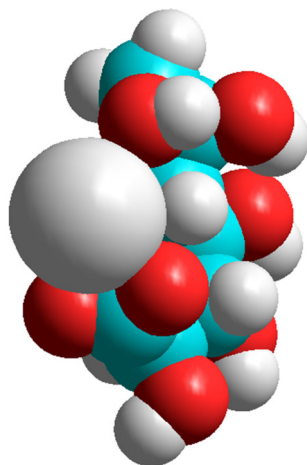
Figure 3: The optimum geometry found to CaHglu$^+$ scorpionate type complex

3.3. Solubility of Ca(OH)$_2$ in caustic liquors and the role of the Gluc$^-$

In the absence of Gluc$^-$, the CaOH$^+$(aq) is the only water soluble calcium species beside the Ca^{2+}(aq) being present in strongly alkaline aqueous solutions.

Due to complex formation between the Ca^{2+} ion and the Gluc$^-$ in caustic solutions, the Ca^{2+} concentration in the equilibrium liquid phase was found to increase with increasing Gluc$^-$ concentration [in the presence of solid Ca(OH)$_2$].

To determine the conditional stability constant of this high–pH calcium–gluconate complex or complexes, the solubility of Ca(OH)$_2$ in sodium hydroxide solutions was first studied, and was found to decrease either by increasing the concentration of NaOH or raising the temperature. Solubility measurements at constant ionic strength [1M (NaCl)] resulted in the experimental data of the solubility product of Ca(OH)$_2$ and the stability constant of CaOH$^+$.

Calculations confirmed that the CaOH$^+$(aq) was the only water soluble calcium species beside the Ca^{2+}(aq) present, and it seems unlikely, that Ca(OH)$_2$(aq) is formed in reasonable quantities in these systems.

3.4. Equilibria in solutions approaching real Bayer conditions

The behavior of the Gluc$^-$ ion in strongly alkaline solution in the presence of Ca^{2+} or Al(OH)$_4^-$ was determined by various techniques.

Beside the CaGluc$^+$ and CaGlucH$_{-1}{}^0$ mononuclear complexes, the Ca$_2$Gluc$_2$H$_{-3}{}^0$ bi- and the Ca$_3$Gluc$_2$H$_{-4}{}^0$ trinuclear complexes are also present in alkaline aqueous solutions containing Ca^{2+} and Gluc$^-$; under these conditions unexpectedly stable complexes are formed via the deprotonation of the alcoholic OH$^-$ on the Gluc$^-$.

The NMR study of the Ca^{2+}/Gluc$^-$ system showed that chemical exchange between the various forms of Gluc$^-$ was slow at low temperatures (0 − 15 °C) and became fast on the NMR time scale above 40−45°C also indicating that the alcoholate groups on both the C2 and C3 carbons participated in Ca^{2+} binding (*Figure 4*).
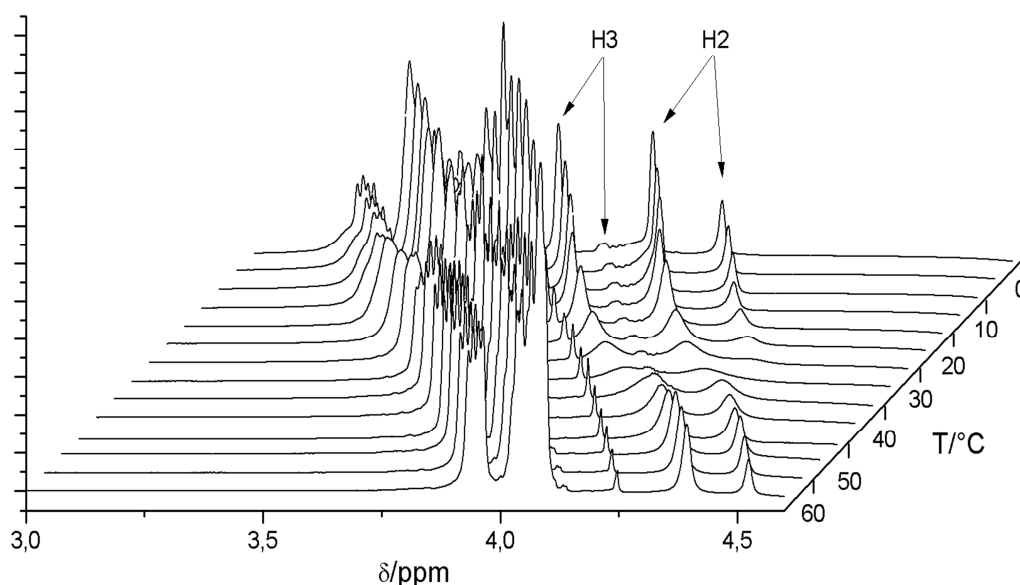

Figure 4: The ^{1}H NMR spectra of the solution containing 0.200 M Gluc$^-$ and 0.080 M Ca^{2+} in the presence of 1.000 M NaOH at different temperatures

Potentiometric titrations on the Ca^{2+}/Gluc$^-$ binary system showed that complexation of Ca^{2+} with Gluc$^-$ in caustic solutions could be reasonably described with four calcium-containing complexes. Beside the formation of the CaGluc$^+$ (log K$_{110}$ = 0.34 ± 0.03) and CaGlucH$_{-1}{}^0$ (log K$_{11-1}$ = −10.97 ± 0.01) 1:1 ratio complexes, two further polynuclear complexes ([Ca$_2$GlucH$_{-3}$]^0 and [Ca$_3$Gluc$_2$H$_{-4}$]^0) must have been assumed. The stability constants of the [Ca$_2$GlucH$_{-3}$]^0 and [Ca$_3$Gluc$_2$H$_{-4}$]^0 complexes are log β$_{22-3}$ = −33.25 ± 0.02 (= 8.03 − 3 · 13.76) and log β$_{32-4}$ = −42.65 ± 0.04 (= 12.39 − 4 · 13.76), respectively. When only mononuclear complexes are formed (pH < 10), two bonding isomers are most likely to coexist in solution. However at pH ≥ 12 the predominant complex formed is the [Ca$_2$GlucH$_{-3}$]^0. At reasonably high concentrations of both the metal ion and the ligand, the trinuclear [Ca$_3$Gluc$_2$H$_{-4}$]^0 complex was formed as follows:

$$\text{CaGlucH}_{-1}{}^0 + [\text{Ca}_2\text{GlucH}_{-3}]^0 \rightleftharpoons [\text{Ca}_3\text{Gluc}_2\text{H}_{-4}]^0$$
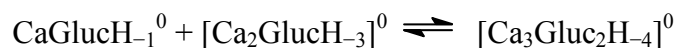
The geometry of the $[\text{Ca}_3\text{Gluc}_2\text{H}_{-4}]^0$ polynuclear complex was optimized by molecular modelling calculations. The resulted structure is presented in *Figure 5*. The central Ca^{2+} entered into bonding interactions with O(C1) and O(C2) of both Gluc⁻ molecules and the remaining two Ca^{2+} atoms form six−membered chelate with the Gluc⁻, respectively, entering into bonding interactions with O(C3) and with the other carboxylic oxygen (O'(C1)).
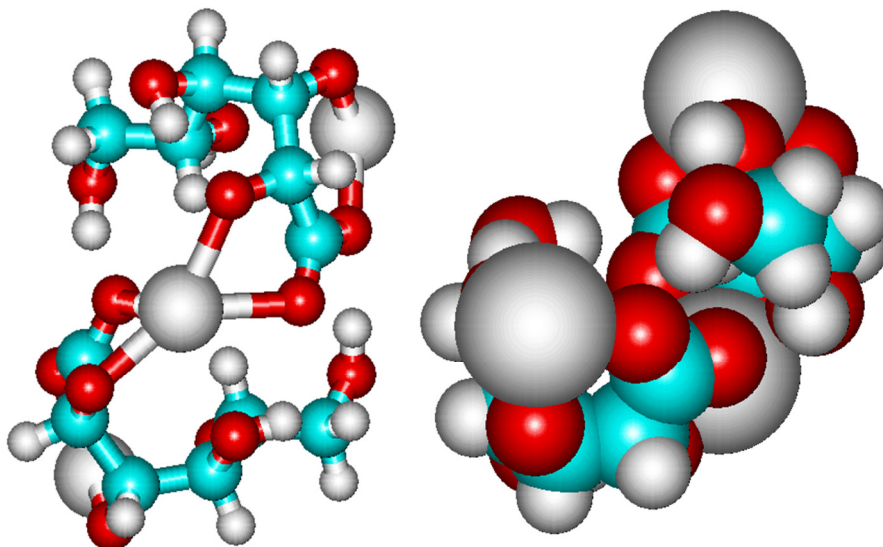

Figure 5: The optimum geometry found for the $[\text{Ca}_3\text{Gluc}_2\text{H}_{-4}]^0$ trinuclear complex with two rendering types (ball-and-stick and spacefilling models)

Binding of the aluminate to gluconate in strongly alkaline solutions (pH > 12) is a pH-independent process (*i.e.* condensation reaction occurs).

The $\text{Al(OH)}_4{}^-$/Gluc⁻ binary system was also investigated. The ¹H and ²⁷Al NMR measurements confirm the complexation between the $\text{Al(OH)}_4{}^-$ and Gluc⁻ unambiguously. The pH potentiometric titration curves were practically identical to those performed in solutions containing Gluc⁻ only. This fact suggests that binding of $\text{Al(OH)}_4{}^-$ to Gluc⁻ in these strongly alkaline solutions (pH > 12) is a pH-independent process. In other words, the (simplified) condensation reaction

$$\text{R−OH} + \text{Al(OH)}_4{}^- \rightleftharpoons \text{R−O−Al(OH)}_3{}^- + \text{H}_2\text{O}$$
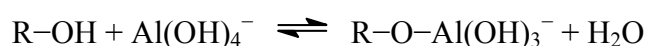
is likely to take place, which does not involve release or uptake of proton. The stability constant of the complex was calculated from NMR spectroscopic measurements as new peaks

emerge in the ^{1}H NMR spectra of the Gluc$^-$ with increasing Al(OH)$_4^-$ concentration and was found to be log K$_{1,1}$ = 2.3 ± 0.4.

In the ternary systems containing Ca^{2+}, Al(III) and Gluc$^-$, beside the calcium−gluconate and Al(III)−gluconate binary complexes the [CaAl(OH)$_4$Gluc]^0, [Ca$_3$Al(OH)$_6$Gluc$_2$]$^+$ and [Ca$_3$Al(OH)$_3$Gluc$_3$]$^{3+}$ are present in solution.

To describe the potentiometric titration curves recorded on the Ca^{2+}/Al(OH)$_4^-$/Gluc$^-$ ternary system, the stability constants calculated previously in the Ca^{2+}/Gluc$^-$ binary systems (OH$^-$, GlucH$_{-1}^{2-}$, CaOH$^+$, GlucH$_{-1}^{2-}$, CaGlucH$_{-1}^0$, [Ca$_2$Gluc$_2$H$_{-3}$]^0 and [Ca$_3$Gluc$_2$H$_{-4}$]^0) were held constant.
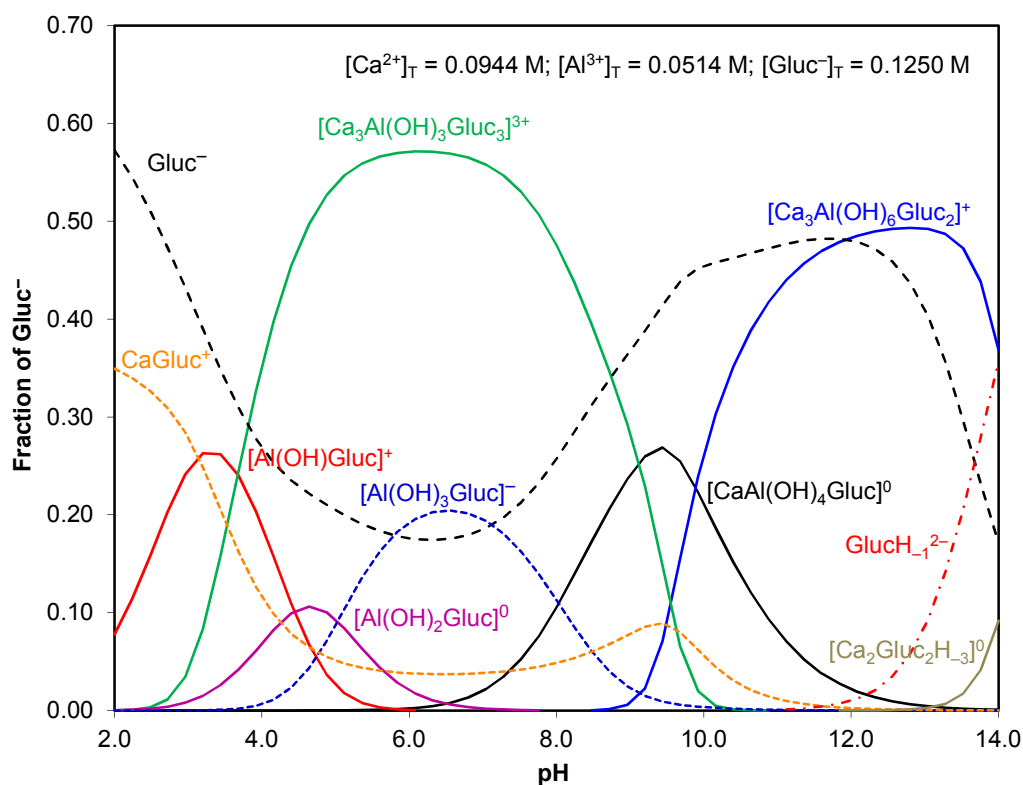

Figure 6: Distribution diagram of the Gluc$^-$ containing complex species in the Ca^{2+}/Al(OH)$_4^-$/Gluc$^-$ ternary system as a function of pH at I = 1 M (NaCl) and 25.0 °C

The stability constant of the CaGluc$^+$ was found to be log K$_{1010}$ = 1.08 ± 0.14, and the species containing Al(III) only were the Al(OH)$_2^+$ (log K$_{010-2}$ = 12.89 ± 0.11), and the Al^{3+} (log K$_{0100}$ = 20.94 ± 0.08) in the solutions. Beside the [Al(OH)$_3$Gluc]$^-$ (log β$_{011-1}$ = 9.89 ± 0.04), [Al(OH)$_2$Gluc]^0 (log β$_{011-2}$ = 15.01 ± 0.07) and [Al(OH)Gluc]$^+$ (log β$_{011-1}$ = 19.54 ± 0.06) binary complexes, the formation of the [CaAl(OH)$_4$Gluc]^0

(log $\beta_{111-4} = 3.76 \pm 0.08$), $[Ca_3Al(OH)_6Gluc_2]^+$ (log $\beta_{312-6} = -11.22 \pm 0.20$) and $[Ca_3Al(OH)_3Gluc_3]^{3+}$ (log $\beta_{313-3} = 18.59 \pm 0.18$) ternary complexes were verified.

The distribution diagram of the calcium containing species extrapolated to the concentration range relevant to the Bayer process ($[OH^-]_T = 2.5$ M, $[Al(OH)_4^-]_T = 2.0$ M, $[Ca^{2+}]_T = 0.34$ mM and $[Gluc^-]_T = 1$ g/dm^3), is presented in *Figure 7*.

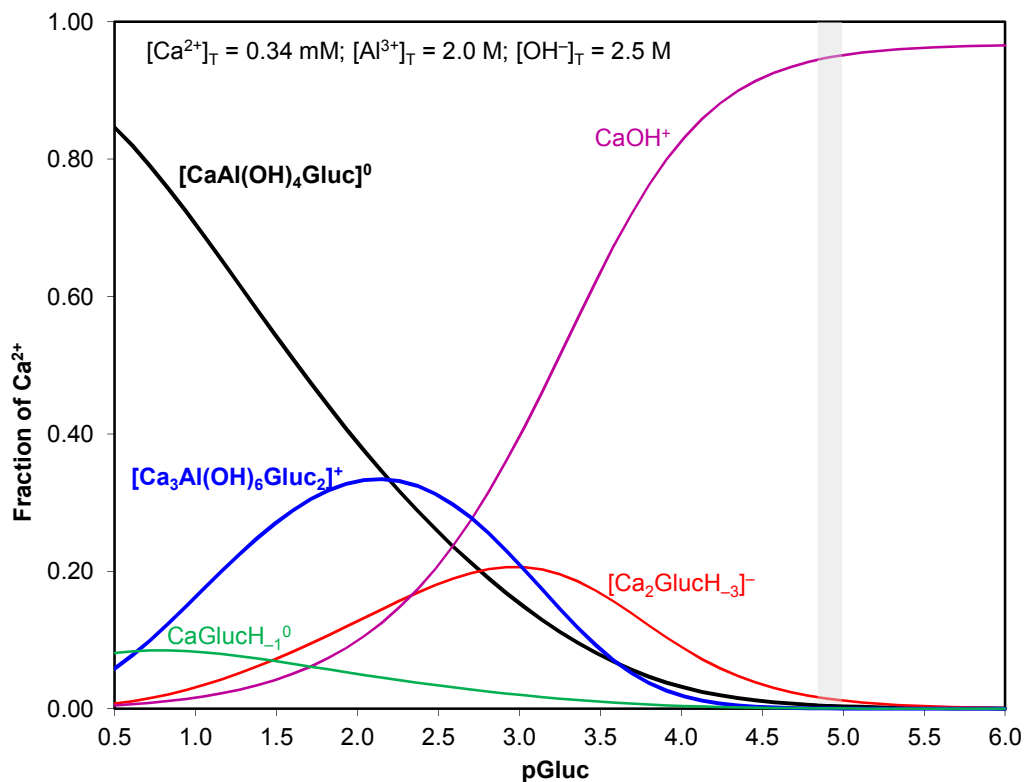*Figure 7: Distribution diagram of the Ca^{2+} containing complex species in the $Ca^{2+}/Al(OH)_4^-/Gluc^-$ ternary system as a function of pGluc. The grey band refers to the $[Gluc^-]_T = 1$ g/dm^3.*

4. Publications

4.1. Journal papers related to the Theses

1. Multinuclear NMR and molecular modelling investigations on the structure and equilibria of complexes forming in aqueous solutions of calcium and gluconate

    A. PALLAGI, P. SEBŐK, P. FORGÓ, T. JAKUSH, I. PÁLINKÓ, P. SIPOS

    Carbohydrate Research 2010. **345 (13).** 1856-1864.

    IF_{2010}: 1.898   IH: 0

2. Structure and equilibria of Ca^{2+}-complexes of glucose and sorbitol from multinuclear (^{1}H, ^{13}C and ^{43}Ca) NMR measurements supplemented with molecular modelling calculations

    A. PALLAGI, CS. DUDÁS, Z. CSENDES, P. FORGÓ, I. PÁLINKÓ, P. SIPOS

    Journal of Molecular Structure 2011. **993 (1–3).** 336-340.

    IF_{2010}: 1.599   IH: 0

3. The solubility of $Ca(OH)_2$ in extremely concentrated NaOH solutions at 25.00 °C

    A. PALLAGI, Á. TASI, A. GÁCSI, M. CSÁTI, I. PÁLINKÓ, G. PEINTLER, P. SIPOS

    Central European Journal of Chemistry 2012. **10(2)**. 332-3370.

    IF_{2010}: 0.991   IH: 0

4.2. Full papers in conference proceedings related to the Theses

1. A glükonát/Ca^{2+} rendszer egyensúlyi kémiája vizes oldatokban *(The equilibrium chemistry of the gluconate/Ca^{2+} system in aqueous solution)*

    A. PALLAGI, P. SEBŐK, I. PÁLINKÓ, P. SIPOS

    XXXII. Kémiai Előadói Napok (Chemistry Lectures), Program és előadásösszefoglalók, ISBN 978-96-3482-969-0, 2009, pp. 169-173.

2. Structural features of some Ca(II)−sugar complexes forming in aqueous solutions studied by NMR spectroscopy and computations

    A. PALLAGI, Z. CSENDES, P. FORGÓ, P. SIPOS, I. PÁLINKÓ

    New Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry, (Melník, M., Segľa, P., Tatarko, M.), ISBN 978-80-227-3509-4, Press of Slovak University of Technology, Bratislava, 2011, pp. 442-451.

4.3. Conference abstracts related to the Theses

1. Structural and equilibrium studies on complexes of Ca^{2+} and gluconate ions in the aqueous phase

   A. PALLAGI, P. SEBŐK, P. FORGÓ, T. JAKUSCH, I. PÁLINKÓ, P. SIPOS

   39th International Conference on Coordination Chemistry, Adelaide, South Australia, 25 − 31 July 2010. (oral presentation)

2. Structural features of Ca^{2+}-carbohydrate solution complexes studied by multinuclear (^{1}H, ^{13}C, ^{43}Ca) NMR spectroscopy

   A. PALLAGI, P. SEBŐK, I. PÁLINKÓ, P. SIPOS

   39TH International Conference on Coordination Chemistry, Adelaide, South Australia, 25 − 31 July 2010. (poster)

3. Structure-reactivity relationship of Ca^{2+}–carbohydrate solution complexes studied by ^{1}H, ^{13}C and ^{43}Ca NMR spectroscopy

   A. PALLAGI, Z. CSENDES, CS. DUDÁS, I. PÁLINKÓ, P. SIPOS

   EUCMOS, Florence, Italy, 29 August − 03 September 2010. (poster)

4. A Ca^{2+} cukorszármazékokkal képzett komplexeinek stabilitása és szerkezete vizes oldatokban

   A. PALLAGI, Z. CSENDES, P. FORGÓ, P. SIPOS, I. PÁLINKÓ

   MKE 1. Nemzeti Konferencia, Sopron, Hungary, 22 − 25 May 2011. (oral presentation)

5. Structural features of some Ca(II)–sugar complexes forming in aqueous solutions studied by NMR spectroscopy and computations

   A. PALLAGI, Z. CSENDES, P. FORGÓ, P. SIPOS, I. PÁLINKÓ

   XXIII. International Conference on Coordination and Bioinorganic Chemistry, Smolenice, Slovakia, 05 − 10 June 2011. (oral presentation)

4.4. Other Journal papers outside the topic of the Theses

1. The effect of particle shape on the activity of nanocrystalline TiO_2 photocatalysts in phenol decomposition

   N. Balázs, K. Mogyorósi, D. F. Srankó, **A. Pallagi**, T. Alapi, A. Oszkó, A. Dombi, P. Sipos

   Applied Catalysis B: Environmental 2008. **84 (3–4).** 356-362.

   IF$_{2008}$: 4.853   IH: 28

2. Synthesis and Structural Features of a Novel Ba(II)-Fe(III)-Layered Double Hydroxide

   D. Srankó, **A. Pallagi**, I. Pálinkó, E. Kuzmann, S. Canton, P. Sipos

   Insights into Coordination, Bioinorganic and Applied Inorganic Chemistry 2009. (Melník, M., Seg'la, P., Tatarko, M.), ISBN 978-80-227-3085-3, Press of Slovak University of Technology, Bratislava, 380-385.

3. Synthesis and properties of novel Ba(II)Fe(III) layered double hydroxides

   D. F. Srankó**, A. Pallagi**, E. Kuzmann, S. E. Canton, M. Walczak, A. Sápi, Á. Kukovecz, Z. Kónya, P. Sipos, I. Pálinkó

   Applied Clay Science 2010. **48 (1-2).** 214-217.

   IF$_{2010}$: 2.303   IH: 2

4. Comparison of the liquid and gas phase photocatalytic activity of flame-synthesized TiO_2 catalysts: the role of surface quality

   N. Balázs, A. Gácsi, **A. Pallagi**, K. Mogyorósi, T. Alapi, P. Sipos, A. Dombi

   Reaction Kinetics Mechanisms and Catalysis 2011. **102 (2).** 283–294.

5. *„Safety first!" Munkavédelem és vörösiszap-kezelés Ausztrália egyik legnagyobb timföldgyárában*

   A. Pallagi

   Magyar Kémikusok Lapja 2011. **6.** 186-187.

full papers, total:	8	related to the topic of the theses:	3
cumulative impact factor, total:	11.644	related to the topic of the theses:	4.448
independent citations, total:	30	related to the topic of the theses:	0