

**STRUCTURE AND EQUILIBRIA OF SOME
Ca(II)-COMPLEXES FORMING IN HYPERALKALINE
AQUEOUS SOLUTIONS**

Ph.D. THESES

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1. Introduction

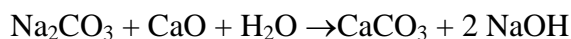
Calcium is the fifth most abundant element on Earth. The aqueous chemistry of calcium is discussed in a considerably large number of literature sources. The published data are mostly concerned with solutions of $\text{pH} < 12$, which are relatively easy-to-handle experimentally. The scarcity of data in the $\text{pH} > 12$ range is understandable on the one hand because highly alkaline (hyper alkaline) solutions pose several difficulties not only in terms of practical aspects of their handling but also in terms approaching them theoretically. However, on the other hand, this is somewhat surprising, given the obvious practical relevance of hyperalkaline solutions containing calcium in, *e.g.*, cement, alumina and paper industry, *etc.*; this would require the accurate knowledge of the physicochemical properties of Ca^{2+} ions (*e.g.*, hydrolysis, complex formation, precipitation, *etc.*) in hypersaline solutions and/or in solutions with extremely high pH-s.

My Ph.D work was carried out in the Material and Solution Structure Research Group (MASOST). In this research group, there are several ongoing research projects focusing on the chemistry of highly alkaline aqueous solutions. In this framework, calcium ions and alkaline solutions are the central themes of my PhD studies.

During my experimental work, at first, the quantitative description of the simplest binary system was attempted comprising the hydrolytic reactions aqueous solutions containing only Ca^{2+} and OH^- . The calcium ions may participate in several reactions in hyper alkaline solution: they can form different ion pairs and solid $\text{Ca}(\text{OH})_{2(\text{s})}$ with OH^- . Such reactions have been studied since 1920s. Even if this is the case, the composition and abundance of the aqueous species, *i.e.*, ion pair(s) forming in solutions are still debated. For describing the $\text{Ca}^{2+}/\text{OH}^-$ binary system, the formation of $\text{CaOH}^+_{(\text{aq})}$ ion pair is commonly accepted in most of the published papers; however, in some references the presence of $\text{Ca}(\text{OH})_2^0_{(\text{aq})}$ is also suggested. Accordingly, in the first part of my work we have attempted to collate and analyze information on the composition(s) and formation constant(s) of the ion pairs forming in this binary system.

In the Bayer alumina production, at various points of the technological process Ca^{2+} ions are added to the highly alkaline reaction mixture consisting of $\text{NaOH}/\text{Al}(\text{OH})_3/\text{H}_2\text{O}$. Accordingly, it was a logical next step to extend our studies to such aqueous solutions. The concentrated caustic solutions used in the alumina refining process readily react with the airborne CO_2 to form Na_2CO_3 . This is an undesirable side

reaction, which may be reverted *via* adding Ca^{2+} ions to the reaction mixture to form CaCO_3 and to regain NaOH . The process is called causticization:



Aluminum ions are present in the Bayer solutions in the form aluminate, $[\text{Al}(\text{OH})_4]^-$ ions. Several literature data are available about the reaction between the Ca^{2+} and aluminate ions: both the formation and interconversion of the various solid phases were the subject of a large number of studies. From the point of view of solution chemistry, no literature data were published on the possible formation of the $[\text{CaAl}(\text{OH})_4]^+$ ion pair. In the Bayer solutions, upon addition of Ca^{2+} ions to the $\text{NaOH}/\text{Al}(\text{OH})_3/\text{H}_2\text{O}$ solutions, hydrocalumite (a layered double hydroxide, $(\text{Ca}_2[\text{Al}(\text{OH})_6]\text{OH})$ type compounds and/or tricalcium aluminate ($\text{Ca}_3\text{Al}_2(\text{OH})_6$, TCA) may be formed. No information could be located in the literature about either the equilibrium (solution) properties of the $[\text{CaAl}(\text{OH})_4]^+$ ion pair or the solubility product of the hydrocalumite-like layered double hydroxide.

The formation of the solid phases mentioned in the previous paragraph is influenced by a plethora of effects. Beside the common physical parameters (*e.g.*, temperature, pressure, *etc.*) the effects exerted by a variety of chemical factors, such as the presence of directly and indirectly introduced inorganic and organic components is also needed to be taken into account. Such compounds are the previously mentioned CO_2 , and various animal and plant degradation products present in the bauxite, *etc.* From these, oxalate, formate, citrate, tartrate, malate and humic acid residues are the most abundant. These compounds may affect a range of technological sub-steps in the alumina refining process, thus the knowledge of their interactions with the other components of the Bayer process solutions is of considerable practical importance. Given that complex formation reactions may take place between the calcium ion and these organic molecules, for further studies, two α -hydroxycarboxylic acids (citrate and tartrate) were selected, both are present in the “real” Bayer solutions. The interactions of Ca^{2+} with these ligands in close-to-neutral solutions are relatively well established, but only scattered information is available on their interaction in strongly alkaline conditions.

2. Aims

The main aim of my Ph.D work was to collect, analyze and interpret information on the complexation interactions of Ca^{2+} ions in hyperalkaline aqueous solutions. My theses comprises of three phases:

First, my aim was to accurately describe the hydrolysis of Ca^{2+} ions in extremely alkaline solutions. In this, we determined the formation constant of the ion pairs forming in solutions and the solubility product of $\text{Ca}(\text{OH})_2$ based on solubility measurement at different ionic strengths and over a range of temperatures.

In the knowledge of the solubility of $\text{Ca}(\text{OH})_2$ in caustic media, in the second phase of my Ph.D work, the aim was the qualitative description of the solubility of $\text{Ca}(\text{OH})_2$ in alkaline solutions containing aluminate. In this part of my work, the solid-phase components, which are in equilibrium with the aluminate solutions, were identified and the solubility product of the main component, the hydrocalumite layered double hydroxide was determined. The other aim was the detection of the possible formation of the $\text{CaAl}(\text{OH})_4^+$ ion pair, and the determination of its formation constant, since the presence of ion pair is expected to cause considerable increase in the solubility of $\text{Ca}(\text{OH})_2$ in such solutions.

In the third phase of my work, the aim was the quantitative description of complex formation between Ca^{2+} and two low molecular weight hydroxyl carboxylic acids in highly caustic solutions. This phase can be separated to two parts. In the first part, description of complex formation between Ca^{2+} and tartrate (Tar^{2-}) ions, in the second, the same with the citrate (Cit^{3-}) ion was the aim. For both ligands, experiments were performed to both qualitatively and quantitatively characterize the complexes formed and to calculate the optimal geometry of the forming complexes.

3. Experimental

For the solubility measurements, a solubility apparatus developed in our research group was used (before the commencement of my Ph.D studies, I participated in the validation experiments of this device). The apparatus is a 15-position thermostable glass bath, which can ensure the simultaneous preparation of several samples. Continuous stirring was provided by a 15 positions *VelpMultistirrer 15* magnetic stirrer. The 50 mL polyethylene reaction vessels were placed inside the glass vessels of the instrument, in which water provided the appropriate heat exchange. The constant $25,0 \pm 0,05$ °C

temperature was provided by a *Julabo F12-MB* heating-cooling thermostat, while the constant $50,0 \pm 0,1$ and $75,0 \pm 0,1$ °C temperatures were assured by an *MLW U2C* thermostat. For measurements carried out at superambient temperatures, the thermostable glass bath was insulated with a polystyrene cover to avoid excessive heat exchange between the glass bath and the environment and to minimize the temperature fluctuation.

The concentrations of Ca^{2+} and Al^{3+} in the supernatants obtained from the solubility measurements were determined by the ICP-OES method using an UNICAM *IRIS Intrepid II XSP Duo* instrument, which allows both axial and radial exposure relative to the plasma. The pulverization of the samples was carried out with a cloud chamber. In this instrument, the plasma burner consists of three concentric quartz tube, where the Ar gas was driven through, both as plasma source and as cooling media. For the measurements, 1350 MHz excitation frequency and 1 L/minute gas flow rate were used. The detector scanned the wavelengths in the visible light range in radial exposure relative to the plasma. Yttrium was used as internal standard.

X-Ray diffractometry measurements were performed using a *Rigaku Miniflex II* diffractometer equipped with CuK_α ($\lambda = 1,5418 \text{ \AA}$) radiation source. Every was measured with $4^\circ/\text{minute}$ ramp speed. The interpretation of the diffractograms was helped by the diffractograms of the pure phases collected from independent measurements.

For the NMR spectroscopic measurements, a *BRUKER Avance DRX 500 NMR* instrument was used. For the ^1H NMR measurements 128 scans, while for the ^{13}C NMR measurements 256 scans were collected for each spectrum.

During the potentiometric measurement, titrations were attempted in caustic media. Here, for well-known reasons, the measurement of the pH using conventional glass electrode is not possible. Thus, for our measurements a platinized platinum indicator electrode (hereafter H_2/Pt electrode) was used, which was in contact with constant (atmospheric) pressure H_2 gas. This electrode can be used beyond the glass electrode's usual range of $1 < \text{pH} < 12$, thus, this electrode could be used for titrations in highly caustic ($\text{pH} > 13$) media. For the titrations with the H_2/Pt electrode, a *Metrohm 888 Titrando* instrument was used. The reference electrode was a commercial, double diffusion layered Ag/AgCl electrode (*Metrohm 6.0750.100*).

For the characterization of complexes forming between Ca^{2+} and the small molecular mass organic ligands in neutral medium, a combined Ca^{2+} ion selective

electrode (Ca-ISE, *Metrohm 6.0510.100*) was employed. The calibration of the electrode was carried out in solutions with neutral pH; the initial Ca^{2+} concentration was 10^{-4} M.

For the determination of the composition and formation constant of various Na-ion pairs, a commercial polymer membrane Na^+ ion selective electrode (Na-ISE) was used; for reference electrode the previously mentioned Ag/AgCl electrode was applied. The calibration of the electrode was carried out in solutions with neutral pH; the ionic strength was set with tetramethylammonium chloride (TMACl). During the calibration, the initial Na^+ concentration was set to 10^{-3} M.

For the freezing-point depression measurements a conventional Beckmann thermometer was used. This type of thermometer can be used for determining minute temperature variations (accuracy $\pm 0,01$ °C) in the temperature range of +2 and -4 °C. The freezing point of distilled water was used as a reference. A mixture of tap water and table salt served as coolant.

For determining the conductivity of the electrolyte solutions, conductometric method was used. From this measurement, the change of conductivity associated with chemical reactions (especially with complex formation reactions) can be measured. For these measurements, a *Jenway 3540* conductometer was applied.

4. Novel scientific results

T1. Via determining the total concentration of Ca^{2+} in NaOH solutions saturated with $\text{Ca(OH)}_{2(s)}$, we proved that in these systems beside the trivial $\text{Ca}^{2+}_{(aq)}$ and $\text{Ca(OH)}^+_{(aq)}$ species, the neutral $\text{Ca(OH)}_{2(aq)}$ complex is also present – a species, which has been neglected in the overwhelming majority of previous works.

Dozens of publications in this field invoked the presence of $\text{CaOH}^+_{(aq)}$ beside the $\text{Ca}^{2+}_{(aq)}$; however, the possible formation of the dissolved $\text{Ca(OH)}_{2(aq)}$ is mentioned only in few references, but its formation constant has not been determined yet.

One consequence of the formation of the neutral, dissolved $\text{Ca(OH)}_{2(aq)}$ is that with increasing the NaOH concentration the total Ca^{2+} concentration cannot be reduced to zero, and that its value asymptotically approaches a minimum (*e.g.*, $[\text{Ca}^{2+}]_{T,\min} = 3 \cdot 10^{-4} \text{ M}$ at $T = 25 \text{ }^\circ\text{C}$).

The assumption that the analytical and equilibrium concentration of NaOH are equal, was proven to be fraudulent at lower NaOH concentrations. We suppose that this false assumption resulted in inaccurate data for the formation constants published in previous works.

T2. The equilibrium constants describing the thermodynamics of the $\text{Ca}^{2+}/\text{OH}^-$ equilibrium system (L , K , β) were determined at 1 M and 4 M ionic strengths. From the temperature dependence of these constants, the thermodynamic data (ΔH , ΔS) could be calculated too.

From the thermodynamic constants obtained, it was deduced that the reactions observed in these systems are entropy driven.

T3. In the $\text{NaOH}/\text{NaAl(OH)}_4/\text{Ca(OH)}_2$ mixtures, at a given temperature and NaOH concentration, there is a maximum NaAl(OH)_4 concentration ($[\text{NaAl(OH)}_4]_{\max}$), below which no alumina-containing solid phase may precipitate from the mixture, and where the equilibrium solid phase is $\text{Ca(OH)}_{2(s)}$.

From $\text{NaOH}/\text{NaAl(OH)}_4/\text{Ca(OH)}_2$ mixtures of various compositions, the precipitating solid phases were identified *via* using XRD method; it was

demonstrated that until a well-defined solution composition was reached, the precipitation of aluminum containing solid phases (*e.g.*, hydrocalumite or TCA) from the solution did not take place.

T4. In the knowledge of the $[\text{NaAl}(\text{OH})_4]_{\text{max}}$ values at a range of solution compositions and temperatures, the solubility product of the solid hydrocalumite hydroxide, $\text{Ca}_2\text{Al}(\text{OH})_6\cdot\text{OH}$ was determined and an upper limit for the formation constant of the $[\text{CaAl}(\text{OH})_4]^+$ ion pair was estimated. To quantitatively describe the speciation of the $\text{NaOH}/\text{NaAl}(\text{OH})_4/\text{Ca}(\text{OH})_2$ systems, the assumption of the $[\text{CaAl}(\text{OH})_4]^+$ is not necessary.

T5. For Tar^{2-} and Cit^{3-} ions, using conductometric titrations, freezing-point depression and NMR spectroscopic measurements, it was proven that in hyperalkaline solutions these ligands formed novel Ca^{2+} -complexes, which were different from those present in systems with neutral pH.

Between Ca^{2+} and Tar^{2-} or Cit^{3-} , hydroxide ion consuming reactions occur in highly caustic aqueous solutions.

These reactions result in significant change in the conductivity of the solution, and decrease the number density of the dissolved species in solution. Moreover, characteristic changes can be observed in the NMR spectra of the ligands consistent with hydroxide ion consumption.

T6. Based on H_2/Pt potentiometric titrations, two novel complex species were identified between Ca^{2+} és Tar^{2-} ions in caustic medium.

It was shown *via* H_2/Pt potentiometric titrations that between Ca^{2+} and Tar^{2-} in caustic media two new, so far unknown complex species ($\text{CaTarH}_{-1}^-(\text{aq})$ and $\text{CaTarH}_{-2}^{2-}(\text{aq})$) were formed, the stability constants of which were found to be $\lg\beta_{11-1} = -11,16 \pm 0,04$ and $\lg\beta_{11-2} = -25,34 \pm 0,03$.

For the determination of these constants, the knowledge of the solubility product of the sparingly soluble $\text{CaTar}_{(\text{s})}$, the formation constants of $\text{TarH}_{-1}^{3-}(\text{aq})$ ion and that of the $\text{NaTar}^-(\text{aq})$ ion pair and the formation constants of $\text{CaTar}^0(\text{aq})$ and $\text{Ca}(\text{Tar})_2^{2-}(\text{aq})$ complexes forming in neutral solutions was necessary. These data were determined from independent measurements.

For the structure of the complexes forming, suggestions were made on the basis of quantum chemical calculations.

T7. From ^1H NMR spectroscopic measurements and from the variations of coupling constants of Cit^{3-} in the presence Ca^{2+} ions, the formation of one new complex ($\text{CaCitH}_{-1}^{2-}(\text{aq})$) in highly caustic solutions was proven. The structure of this new complex was determined *via* using quantum chemical calculations.

Based on freezing-point depression and Na-ISE potentiometric measurements, it was proven that significant ion pair formation took place between the Na^+ and the Cit^{3-} ions. It was also proven that the formation of Na^+ ion pairs at high ionic strength could suppress the formation of Ca complexes in highly caustic solutions verified by ^1H NMR measurements.

5. Potential applications of the results

The results presented in this dissertation are mainly of fundamental type. In spite of this, some of the observations presented here may have potential industrial applications both directly and indirectly. For example, in the technology of the Bayer alumina processing, it is a well-known observation that there is always a non-removable (remnant) Ca^{2+} ion concentration in solutions even at the highest possible caustic concentrations. Our results are in line with this “insider” industrial observation, while the data published by others (where the formation of the $\text{Ca}(\text{OH})_{2(\text{aq})}$ species was not taken into account) this observation was not confirmed. Hydrocalumite is known to be an unstable intermediate in the Bayer alumina process; the knowledge of its solubility product can be of use in various industrial process optimization steps. The “non-formation” of the $[\text{CaAl}(\text{OH})_4]^+$ ion pair is of importance in the thermodynamic modeling of the Bayer solutions. The tartrate and citrate ions are major organic pollutants in “real” Bayer solutions. Based on our results, under typical Bayer circumstances, they are primarily present in the forms of Na^+ ion pairs.

6. Publications and conference presentations

MTMT identifier: 10029316

6.1. Papers related to the Theses and published in refereed journals

1. **Gácsi A.**, Kutus B., Buckó Á., Csendes Z., Peintler G., Pálínkó I., Sipos P.
Some aspects of the aqueous solution chemistry of the $\text{Na}^+/\text{Ca}^{2+}/\text{OH}^-/\text{Cit}^{3-}$ system:
The structure of calcium citrate complex forming in hyperalkaline aqueous
solution
Journal of Molecular Structure **1118** (2016) 110–116. IF₂₀₁₅: 1,780
2. **Gácsi A.**, Kutus B., Kónya Z., Kukovecz Á., Pálínkó I., Sipos P.
Estimation of the solubility product of hydrocalumite-hydroxide, a layered double
hydroxide with the formula of $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{OH}\cdot n\text{H}_2\text{O}$
Journal of Physics and Chemistry of Solids **98** (2016) 167–173. IF₂₀₁₅: 2,048
3. Kutus B., **Gácsi A.**, Pallagi A., Pálínkó I., Peintler G., Sipos P.
A comprehensive study on the dominant formation of the dissolved $\text{Ca}(\text{OH})_{2(\text{aq})}$ in
strongly alkaline solutions saturated by Ca(II)
RSC Advances **6** (2016) 45231–45240. IF₂₀₁₅: 3,289
4. **Gácsi A.**, Kutus B., Csendes Z., Faragó T., Peintler G., Pálínkó I., Sipos P.
Formation and structure of calcium L-tartrate complexes in hyperalkaline
solutions
Dalton Transactions **45** (2016) 17296–17303. IF₂₀₁₅: 4,177

6.2. Papers related to the Theses published as full papers or abstracts in conference and other proceedings

1. **Gácsi A.**, Kutus B., Béltéki R., Gyulavári T., Cseh A., Pálínkó I., Sipos P.
Determining of the solubility product of CaAl-layered double hydroxide,
18th International Symposium in Intercalation Compounds (2015) 114.
(abstract in English)

2. **Gácsi A.**, Kutus B., Bruszel B., Peintler G., Pálínkó I., Sipos P.
Complex formation between Ca(II) and simple organic ligands (citrate and tartrate) in hyperalkaline aqueous solutions
34th International Conference on Solution Chemistry (2015) 34.
(abstract in English)
3. **Gácsi A.**, Kutus B., Cseh A., Béltéki R., Gyulavári T., Bárdos E., Pálínkó I., Sipos P.
Formation of Ca-Al containing layered double hydroxides and its solubility product determination in highly caustic solutions
NanoOstrava 2015, 4th Nanomaterials and Nanotechnology Meeting (2015) 157.
(abstract in English)
4. Kutus B., **Gácsi A.**, Pallagi A., Pálínkó I., Sipos P., Peintler G.
Comprehensive study on the dissolved Ca(OH)₂ in strongly alkaline solutions
10th International Alumina Quality Workshop 19–23 April 2015 Perth Western Australia (2015) 285–289.
(full paper in English)
5. **Gácsi A.**, Bruszel B., Suba N., Csendes Z., Kutus B., Peintler G., Pálínkó I., Sipos P.
Studies on the structure of Ca²⁺ complexes with tartrate and citrate in hyperalkaline solutions with ¹H NMR spectroscopy
XII. International Congress of Young Chemists: YoungChem 2014 (2014) 83.
(abstract in English)
6. Pallagi A., Peintler G., **Gácsi A.**, Kutus B., Pálínkó I., Sipos P.
The importance of the dissolved Ca(OH)_{2(aq)} in highly alkaline solutions
16th International Symposium on Solubility Phenomena and Related Equilibrium Processes (2014) 95.
(abstract in English)
7. Bruszel B., **Gácsi A.**, Suba N., Csendes Z., Pálínkó I., Sipos P.
Kalcium(II)-ion hidroxikarbonsav komplexeinek NMR szerkezetvizsgálata erősen lúgos közegben
XXXVII. Kémiai Előadói Napok (2014) 48–52.
(full paper in Hungarian)
8. **Gácsi A.**, Pallagi A., Bajnóczi É.G., Pálínkó I., Peintler G., Canton S.E., Sipos P.

The temperature dependence of Ca(II) solubility in strongly alkaline aqueous solutions

Monograph Series of the International Conferences on Coordination and Bioinorganic Chemistry **11** (2013) 58–62, ISBN:978-80-227-3918-4.

(full paper in English)

6.3. Other papers published in refereed journals

1. Balázs N., **Gácsi A.**, Pallagi A., Mogyorósi K., Alapi T., Sipos P.
Comparison of the liquid and gas phase photocatalytic activity of flame-synthesized TiO₂ catalysts: the role of surface quality
Reaction Kinetics, Mechanisms and Catalysis **102** (2011) 283–294. IF₂₀₁₅: 1,265
2. Pallagi A., Tasi Á., **Gácsi A.**, Csáti M., Pálinkó I., Sipos P.
The solubility of Ca(OH)₂ in extremely concentrated NaOH solutions at 25.00 °C
Central European Journal of Chemistry **10** (2012) 332–337. IF₂₀₁₅: 1,329

6.4. Other papers published as book chapter

1. Veréb G, Ambrus Z, **Gácsi A.**
Removal of organic compounds in water by photocatalysis in flow reactor
Vizek szerves szennyezőinek eltávolítása nagyhatékonyságú oxidációs módszerekkel: *Removal of organic contaminants of waters by advanced oxidation processes* (2010) 161–171, ISBN:978-963-06-9621-0.

6.5. Other full papers or abstracts published in conference proceedings

1. **Gácsi A.**, Pallagi A., Tasi Á.G., Peintler G., Pálinkó I., Sipos P.
A kalcium-hidroxid oldhatósága lúgos és extrém lúgos közegben 25 és 50 °C-on
XXXIV. Kémiai Előadói Napok (Chemistry Lectures): Program és előadásösszefoglalók (2011) 125–129.

(full paper in Hungarian)

2. Pallagi A., **Gácsi A.**, Kutus B., Peintler G., Pálinkó I., Sipos P.
A kalcium hidroxidjai erősen alkalikus körülmények között, valamint ezek hatása a terner rendszerek egyensúlyaira
XXXVII. Kémiai Előadói Napok (2014) 51.
(abstract in Hungarian)
3. Pallagi A., **Gácsi A.**, Bajnóczi É., Kutus B., Tasi Á., Peintler G., Berkesi O., Pálinkó I., Sipos P.
Ca(II) complexation in hyperalkaline aqueous solutions – relevance in the Bayer process and in the safety of radioactive waste repositories
48. Komplexkémiai Kollokvium (2014) E29.
(abstract in Hungarian)
4. Pallagi A., Peintler G., **Gácsi A.**, Kutus B., Pálinkó I., Sipos P.
Az oldott $\text{Ca}(\text{OH})_2$ jelentősége erősen lúgos oldatokban
48. Komplexkémiai Kollokvium (2014) E45.
(abstract in Hungarian)

Data on the scientific achievements

Full journal papers, total: 6	related to the topic of the Theses: 4
Cumulative impact factor, total: 13.888	related to the topic of the Theses: 11.294
Independent citations, total: 14	related to the topic of the Theses: 1