

Complex equilibria in strongly alkaline aqueous solutions containing Ca(II), Al(III) and heptagluconate ions

Ph.D. Theses



Ákos Buckó

Supervisors: Prof. Pál Sipos
Prof. István Pálinkó

Doctoral School of Chemistry

Department of Inorganic and Analytical Chemistry,
Faculty of Science and Informatics, University of Szeged

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Introduction

The interactions of sugar carboxylates with various metal ions have been extensively studied since the very beginning of the last century owing to their widespread applications in industrial processes.

Two prominent members of these compounds, namely D-gluconic (GlucH) and D-heptagluconic acids (HpgIH), find application in the food industry as leavening, flavoring or fat absorption reducing agents, while their sodium salts are often utilized as metal chelators for a wide range of medical and industrial purposes.

Small-molecular-weight organic substances, being common constituents of most bauxite ores, are introduced to the Bayer process upon the digestion of raw bauxite. According to the literature, they can form highly stable multinuclear complexes with Ca^{2+} ions in strongly alkaline medium. Thus, their presence can greatly affect the solubility of $\text{Ca}(\text{OH})_2(\text{s})$, which is used for NaOH recovery in the so-called recausticization process. Besides their incidental accumulation, these organic compounds sometimes are added intentionally to the process liquor to inhibit the extensive formation of undesired by-products, such as the well-known tricalcium-aluminate, by driving the reaction towards the formation of $\text{CaCO}_3(\text{s})$.

From a process optimization perspective, the interactions of sugar carboxylates with Al^{3+} ions should also be considered. Until now, the vast majority of previous research dealt only with complexation reactions taking place in acidic to slightly alkaline pH regime ($\text{pH} < 12$), which requires conventional methodology and experimentation.

Based on the results reported for systems containing not only Ca^{2+} but also other metal ions, sugar carboxylates have a high tendency to form heteropolynuclear species, $\text{Ca}_p\text{M}_q\text{L}_r^{2p+xq-r}$, where M represents another tri- (Al^{3+} , Fe^{3+} , $x = 3$) or tetravalent (Th^{4+} , $x = 4$) metal ion, and L stands for the ligand containing OH and COO^- groups.

Aims of the work

For effective optimization of an industrial process, adequate knowledge regarding the boundary conditions where these ternary complexes tend to form is indispensable. Therefore, our aim was to determine the composition and stability constants of the complexes forming between HpgI^- , Ca^{2+} and Al^{3+} ions in a wide range of pH (2–12), with special emphasis on interactions occurring in the strongly alkaline medium. Along with the description of the

solution equilibria prevailing in the ternary systems and the corresponding binary sub-systems, we also attempted to extrapolate the equilibrium data to elevated temperatures and high ionic strengths relevant to industrial conditions. Finally, we performed a comprehensive characterization of the solid phases precipitated from aqueous solutions.

Experimental

The protonation constant of Hpgl^- was determined by pH potentiometric titrations employing glass electrode, whereas the deprotonation of both Gluc^- and Hpgl^- ions was monitored using H_2/Pt electrode. The latter reaction was probed by ^{13}C nuclear magnetic resonance (NMR) spectroscopy as well.

To quantify the complex formation equilibria for the binary and ternary systems, potentiometry was applied using again a H_2/Pt electrode. Additionally, the thus obtained data were supplemented by polarimetric measurements, and the corresponding formation constants were obtained by simultaneously fitting both cell potentials and optical rotations assuming different speciation models. Furthermore, electrospray ionization mass spectrometric (ESI-MS), freezing point depression and solubility measurements were used to validate the proposed model. The metal-ion binding sites as well as the possible structure of the complexes in solution were scrutinized by means of ^1H and ^{13}C NMR spectroscopic techniques.

The various solid phases that were observed to precipitate at certain well-defined solution compositions were investigated with a set of experimental tools: the crystallinity and morphology along with the elemental distribution were characterized by X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analysis. The information on the possible structure of these compounds were obtained by Raman and infrared (IR) spectroscopies. The amount of Ca^{2+} and Al^{3+} was determined by inductively coupled plasma optical emission spectrometry (ICP-OES), whereas the concentration of the ligand in each sample was calculated based on UV-vis spectrophotometric measurements. Finally, the thermal properties of the solids were studied using differential thermogravimetric analysis (DTG) coupled with IR spectroscopy, in order to identify the processes associated with each mass loss.

New scientific results

T1. It has been demonstrated that Gluc^- undergoes two consecutive deprotonation steps, yielding GlucH_1^{2-} and GlucH_2^{3-} species.

The two stepwise acid dissociation constants were determined from fitting the ^{13}C NMR chemical shifts assuming the two underlying equilibria. Although the first deprotonation step was sufficient to describe most of the observed variations, it was necessary to assume the formation of the GlucH_2^{3-} species to obtain satisfactory agreement between the simulated and measured data in the strongly alkaline region. Although the formation of the latter was only around $\approx 30\%$, the existence of this species was supported by matrix-rank analysis as an independent numerical method.

T2. It was shown that in strongly alkaline solutions, the composition of highly stable polynuclear Ca - Gluc^- complexes remains identical in a wide range of temperature.

Based on the results of potentiometric titrations performed at $t = 25, 50$ and $75\text{ }^\circ\text{C}$, the calculated speciation remained intact on all three temperature steps, with $\text{Ca}_3\text{Gluc}_2(\text{OH})_4^0$ being the predominant species. This finding is in line with the titration curves obtained, which remained nearly identical on all three temperatures.

T3. A set of novel coordination compounds were found to be formed between aluminum and heptagluconate ions both in acidic and in strongly alkaline aqueous solutions.

Potentiometric titrations and polarimetric measurements conducted from pH 1 to 14 revealed the formation of several hitherto unknown complex species. Besides the mononuclear 1:1 complex already known in the literature, the formation of the $\text{Al}(\text{OH})_5\text{Hpgl}^{3-}$, $\text{Al}(\text{OH})_5\text{Hpgl}_2^{4-}$, $\text{Al}_4(\text{OH})_{15}\text{Hpgl}_3^{6-}$ as well as the $\text{Al}_3(\text{OH})_{13}\text{Hpgl}_2^{6-}$ complexes has been established, the latter being the prevalent species in the strongly alkaline region.

Furthermore, below $\text{pH} = 6$ two dimers of the monomeric $\text{Al}(\text{OH})_2\text{Hpgl}^0$ species, the $\text{Al}_2(\text{OH})_4\text{Hpgl}_2^0$ complex and its deprotonated form, $\text{Al}_2(\text{OH})_5\text{Hpgl}_2^-$ were detected.

T4. It was found that the species forming between aluminate and heptagluconate ions in the neutral pH range are likely to be ligand-stabilized hydroxides.

According to the results of ^1H and ^{13}C NMR experiments conducted at $\text{pH} = 4, 8$ and 12 , the spectra obtained at $\text{pH} = 8$ were nearly identical of that of the plain ligand indicating the lack of substantial structural change of Hpgl^- upon metal-ion association. This proposition was supported by semi-quantitative solubility simulations: as for the pH range of 6–11, the total

concentrations of Al^{3+} and OH^- ions exceeded the solubility product of $\text{Al}(\text{OH})_3(\text{s})$, yet no precipitation could be observed in the presence of heptagluconate ions.

T5. It was proven that Hpgl^- ions form ternary complexes with Ca^{2+} , Al^{3+} ions in strongly alkaline aqueous solutions. Assuming only the binary $\text{Ca}^{2+}/\text{Hpgl}^-$ and $\text{Al}^{3+}/\text{Hpgl}^-$ complexes was not sufficient to describe the corresponding solution equilibria.

The results obtained from potentiometric titrations provided strong evidence for the formation of ternary complexes in the pH range of 8–14, whereas at $\text{pH} < 8$, the inclusion of binary complexes was adequate to fit the measured data. Besides the various protonated forms of the $\text{CaAl}(\text{OH})_4\text{Hpgl}_2^-$ species, complexes with 1:2:2, 2:1:2, 2:2:2 and even 3:1:4 stoichiometries were determined. These findings have been qualitatively confirmed by the ^1H and ^{13}C NMR spectroscopic experiments: the spectra of Hpgl^- recorded in the presence of Ca^{2+} and $\text{Al}(\text{OH})_4^-$ displayed substantial differences (*i.e.*, number and position of peaks, spectrum shape) as compared to the spectra observed in the case of the binary samples. According to the Ca^{2+} -dependent NMR series, at least three different ternary complexes could be inferred, in line with the simulated concentration distribution diagrams.

T6. It has been established that the compositions of the solid ternary complexes precipitated from Ca^{2+} -, Al^{3+} - and Hpgl^- -containing solutions are $\text{CaAlHpgl}(\text{OH})_4^0$ and $\text{Ca}_2\text{AlHpgl}_2(\text{OH})_5^0$ above $n_{\text{OH}}/n_{\text{Hpgl}} = 1.0$ ratio, while $\text{Ca}_3\text{Al}_2\text{Hpgl}_3(\text{OH})_9^0$ is formed exclusively below this ratio.

Based on ICP-OES and UV-vis measurements, two uniform groups of ternary complexes could be distinguished, while for the binary complexes, the formation of $\text{Al}_3\text{Hpgl}(\text{OH})_8^0$ and various mixed Ca-containing complexes was invoked. These results were reinforced by IR and Raman spectroscopic measurements: Fourier self-deconvolution of the individual carboxylate bands of the complexes indicated that the coordination of the ligand to Ca^{2+} and Al^{3+} ions in the ternary solids differ from its binding in the binary complexes.

T7. It was found that the thermal stability of binary and ternary complexes of heptagluconate was significantly higher than that of its commercially available salts.

Based on the IR spectra recorded for samples calcined at different temperatures, an increase in the temperature associated with the onset of degradation could be observed in the following order: NaHpgl and CaHpgl_2 salts $<$ Al-Hpgl complex \approx Ca-Hpgl complexes $<$ ternary complexes. The outstanding thermal stability of ternary complexes was attributed to the simultaneous binding of both metal ions to the ligand(s), implying the presence of stronger chelate structures.

Practical applications

As discussed above, our main goal was to provide a comprehensive overview on a complicated three-component equilibrium system, which may serve as a good starting point for future optimization attempts regarding the Bayer process. Namely, our results may contribute to a better understanding of the complexation reactions taking place in Bayer liquors, in particular by providing a basis for the quantitative description of the corresponding equilibria. Furthermore, the implications regarding the structure of the complexes may provide new insights into the underlying mechanism and the role of different molecular motifs in metal-ion coordination.

Publications and conference participations

Full papers directly related to the theses published in peer-reviewed journals:

1. **Buckó Á.**; Kása Zs.; Szabados M.; Kutus B.; Berkesi O.; Kónya Z.; Kukovecz Á.; Sipos P.; Pálinkó I. The structure and thermal properties of solid ternary compounds forming with Ca^{2+} , Al^{3+} and heptagluconate ions. *Molecules* **2020**, 25(20), 4715, 14 p.
Impact factor (2019): 3.267
2. **Buckó, Á.**; Kutus, B.; Peintler, G.; Kele, Z.; Pálinkó, I.; Sipos, P. Stability and Structural Aspects of Complexes Forming between Aluminum (III) and D-Heptagluconate in Acidic to Strongly Alkaline Media: An Unexpected Diversity. *J. Mol. Liq.* **2020**, 113645.
Impact factor (2020): 5.065
3. **Buckó, Á.**; Kutus, B.; Peintler, G.; Pálinkó, I.; Sipos, P. Temperature Dependence of the Acid–Base and Ca^{2+} -Complexation Equilibria of d-Gluconate in Hyperalkaline Aqueous Solutions. *Polyhedron* **2019**, 158, 117–124, doi:10.1016/j.poly.2018.10.034.
Impact factor (2019): 2.343

Full papers directly related to the theses published in conference proceedings:

1. **Buckó, Á.**; Kutus, B.; Peintler, G.; Sipos, P.; Pálinkó, I. Complexation of heptagluconate with aluminate ions in strongly alkaline aqueous solutions. Melnik, M; Segl'a, P; Tatarko, M. *Progressive Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry*: Slovak Chemical Society, **2019** pp. 24-30.
2. **Buckó, Á.**; Kutus, B.; Peintler, G.; Pálinkó, I.; Sipos, P. Temperature dependence of proton dissociation and complexation processes in the Ca²⁺/gluconate system under hyperalkaline conditions. Melník, M; Segl'a, P; Tatarko, M. *Modern Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry*: Slovak Chemical Society, **2017** pp. 27-36.

Full papers not directly related to the theses published in peer-reviewed journals:

1. Kutus, B.; Peintler, G.; **Buckó, Á.**; Balla, Zs.; Lupan, A.; Attia, AAA.; Pálinkó, I.; Sipos, P. The acidity and self-catalyzed lactonization of L-gulonic acid: thermodynamic, kinetic and computational study. *Carbohydr. Res.* **2018**, 467, pp. 14-22.
Impact factor (2016) : 2.096
2. Gácsi, A.; Kutus, B.; **Buckó, Á.**; Csendes, Z.; Peintler, G.; Pálinkó, I.; Sipos, P. Some aspects of the aqueous solution chemistry of the Na⁺/Ca²⁺/OH⁻/Cit³⁻ system: The structure of calcium citrate complex forming in hyperalkaline aqueous solution. *J. Mol. Struc.* **2016**, 1118, pp. 110-116.
Impact factor (2016): 1.753
3. Kutus, B.; **Buckó, Á.**; Peintler, G.; Pálinkó, I.; Sipos, P. Calcium complexation and acid-base properties of L-gulonate, a diastereomer of D-gluconate. *Dalton Trans.* **2016**, 45 pp. 18281-18291.
Impact factor (2016): 4.029

Other full papers not directly related to the theses published in conference proceedings:

1. Dudás, Cs.; Kutus, B.; **Buckó, Á.**; Böszörményi, É.; Faragó, T.; Peintler, G.; Pálinkó, I.; Sipos, P. Small Mw hydroxy- and oxocarboxylate type organics relevant to the Bayer process - acid-base properties and calcium-complexation in moderately to highly alkaline medium.
Canfell, A; Ladhams, M. *Alumina2018: The 11th AQW International Conference - Conference Proceedings*: AQW Inc., **2018** pp. 381-386.
2. **Buckó, Á.**; Kutus, B.; Peintler, G.; Pálinkó, I.; Sipos, P. Az L-gulonát ion protonálódásának és laktonizációjának vizsgálata.
Bohner, B.; Mesterházy, E. *XXXVIII. Kémiai Előadói Napok Program és előadás-összefoglalók*: Szegedi Tudományegyetem, **2015**, ISBN 978-963-9970-64-9

Other conference participations:

Co-author of 9 lectures presented in international conferences

Co-author of 4 lectures presented in Hungarian conferences

Co-author of 2 posters presented in international conferences

Full papers published in peer-reviewed journals:

Theses related: 3

Total: 9

Cumulative impact factor:

Theses related: 10.675

Total: 18.553