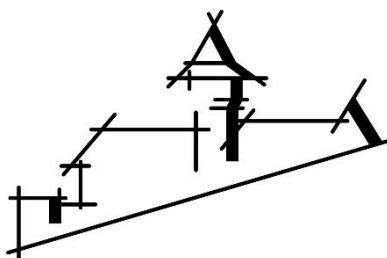# PROGRESSIVE TRENDS IN COORDINATION, BIOINORGANIC, AND APPLIED INORGANIC CHEMISTRY

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Complexation of heptagluconate with aluminate ions in strongly alkaline aqueous solutions

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The complex formation of sugar-type ligands in alkaline aqueous solutions, such as α-D-heptagluconate (Hpgl⁻) with a tri- or tetravalent cations (*e.g.* B(III), Fe(III), Al(III), lanthanides like Nd(III) or Eu(III) and actinides like Th(IV) or Cm(III)) are of relevance in certain types of radioactive waste repositories as well as in hydrometallurgical extraction of metals. Al(III) is a typical "hard" type metal ion, preferring thus coordination to O-donors, such as carboxylates and alcoholates. The interactions of Al(III) with the analogous D-gluconate were studied before. In earlier papers, only the existence of 1:1 complex was assumed [1]. However, in recent investigations with other trivalent cations (Fe(III), lanthanides) the formation of bis (1:2) complexes was reported [2]. Furthermore, results with Th(IV) and Al(III) indicate, that the involvement of Ca(II) may enhance the stability of complexes *via* the formation of ternary (heteropolynuclear) $Ca_pM_qL_r$ complexes [3, 4].

Although some structural information of these mixed-metal complexes may have been known from the literature, the information on equilibrium properties, composition of the complexes and the boundary conditions (at which these species tend to form) is very scarce. In order to elucidate the solution equilibria in the $Ca^{2+} - Al(OH)_4^- - Hpgl^-$ ternary system, the respective binary systems must be investigated first. Therefore, our main goal was to unfold the speciation in the $Al(OH)_4^- - Hpgl^-$ system in hyperalkaline media.

In this current work, the solution species have been investigated *via* polarimetric measurements and pH-potentiometric titrations using H_2/Pt electrode.

INTRODUCTION

The interaction between carbohydrate derivatives, such as sugar acids, and metals have been studied extensively for their essential role in both enzymatic reactions in living organisms and in industrial processes. Polyhydroxy carboxylates are considered as effective chelating agents due to the presence of both carboxylic and hydroxy groups. This property is commonly utilized in pharmaceutical industry, where the complexes of these ligands with various essential metal ions (*e.g.* calcium, iron, zinc) are used to treat metal deficiency diseases. Furthermore, in metallurgy they can serve as excellent cleaning and derusting agents or as an additive in cementitious materials for its ability to regulate the setting time and water resistance of concrete [5].

During the establishment of underground repositories to deposit low and intermediate level radioactive waste (L/ILW), their interactions with lanthanides and actinides must be considered for safety reasons. For these types of vaults, a cement matrix is used to solidify the waste components. It is assumed, that

the incidental intrusion of water alters the cementitious material, forming hypersaline pore water, therefore varying the pH from 7 to 13 during cement degradation. Since some of these ligands are ingredients of Portland cement, they are likely to be present in these systems and interact with radionuclides through complexation, consequently mobilizing them. For these reasons the fundamental thermodynamic description of the co-existing liquid and solid species over long-time scales are of interest [6].

Sugar-type ligands could be present in strongly caustic Bayer liquors, where the solubility of $Ca(OH)_2$ could be affected by these complexing agents [7]. D-gluconate ($Gluc^-$), being a cheap, prominent member of the hydroxy carboxylates, is used as a model compound for investigating the interactions between sugar carboxylates and metals. $Gluc^-$ is a well-known inhibitor of gibbsite ($Al(OH)_3 \cdot 3H_2O$) precipitation. Earlier results suggested the lack of complexation between aluminate and $Gluc^-$ in solutions with pH > 13 [1]. However, recent publications on the topic confirmed, that $Gluc^-$ does form complexes with aluminate ($logK_{11} = 2.4\pm0.4$) though the process was proven to be pH-independent [8]. On the other hand, in systems containing Ca^{2+}, $Gluc^-$ and Fe^{3+} the solution equilibria were observed to be slow, warranting further experimental work [9]. These yet unsolved contradictions indicate, that the quantitative description of the species formed between Ca^{2+}, Al^{3+} and sugar-carboxylates is still inadequate.
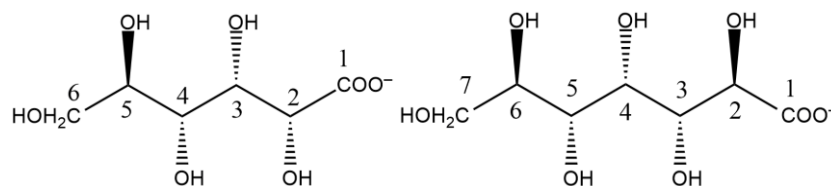

Figure 1: Structural formulae of D-gluconate (left) and D-heptagluconate (right)

Finally, there is very few information on the effect of stereochemistry of these type of ligands in the literature. In earlier papers published in our group, it was found that in case of complexation with calcium ions, the arrangement of OH^- groups might have a decisive impact on the speciation, resulting particles of similar composition. Accordingly, the difference in the composition of the forming complexes, upon comparison of D-gluconate and D-heptagluconate ($Hpgl^-$), lies in that the alcoholic OH^- groups C2-OH and C3-OH are in *threo* configuration in the case of $Hpgl^-$. This results the coordination of COO^- and the two subsequent alcoholic OH^- groups for Gluc–, otherwise the coordination *via* C4-OH was more favorable instead of C3-OH [10]. Such studies are of importance, as they may reveal the possible role of the configuration of the ligand during complex formation. Therefore, we embarked on a research to unravel these quite diverse results: We chose D-heptagluconate as model ligand, and our main tool was polarimetry, enhanced with pH-potentiometry.

EXPERIMENTAL PART

Reagents and solutions

Stock solutions from each compound were prepared using anhydrous sodium heptagluconate ($Hpgl^-$; Sigma-Aldrich product, ≥99% purity), sodium chloride (VWR product, analytical reagent grade) and sodium hydroxide (VWR, analytical reagent grade). Reagents were dissolved in MilliQ Millipore water. Carbonate-free NaOH solution was prepared and standardized as described previously [11]. The stock

$Al(OH)_4^-$ solution was prepared according to procedures described earlier [12], *i.e.*, by dissolving 99.9% pure aluminum shots (Alfa Aesar) in a standardized and carbonate-free NaOH solution. The aluminum shots (50.964 g) were slowly added to the thermostated carbonate-free NaOH solution (500 cm^3; 8.0 M) and the mixture was continuously stirred with a magnetic stirrer under an Allihn condenser equipped with soda lime containing a drying tube. Dissolution of the aluminum shots needed 4–5 days under these conditions. The mass loss was found to be 7–8 g including 6.0 g of H_2 formation. The prepared Na-aluminate solution was filtered, and the exact density of the Na-aluminate (1.4163 g cm^{-3}; 4.3097 M) solution was determined by a 25 cm^3 volume pycnometer at 25.0 ± 0.1 °C.

Potentiometric titrations
Potentiometric titrations were performed using a Metrohm 888 Titrando instrument. Custom made glass cells (max. volume 120 cm^3) for the titrations were externally thermostated to 25.00±0.04°C.
The measurements were carried out using a H_2/Pt electrode, which was prepared according to the instructions described in the literature [13]. Full electrochemical cell consisted of a platinized-platinum hydrogen electrode and a thermodynamic Ag/AgCl reference electrode, and was constructed as follows:

$$H_2/Pt \mid \text{test solution, I} = 4 \text{ M (NaCl)} \parallel 4 \text{ M NaCl} \mid 4 \text{ M NaCl, Ag/AgCl} \qquad (1)$$

Potentiometric titrations with systems containing both, $Al(OH)_4^-$ and Hpgl$^-$, were performed with 0.200 M initial NaOH concentration of each titrated solution. The titrant was 0.9889 M HCl and the ionic strength was set to 5.0 M with NaCl. The starting volume was 70 cm^3 and a maximum of 30 cm^3 titrant was added in each case. The [Hpgl$^-$]$_T$ concentration (hereafter the T in subscription denotes total or analytical concentration) was varied between 0.100 –0.400 M; the [$Al(OH)_4^-$]$_T$ concentration was set to 0.200 M. During the other set of measurement, the [Hpgl$^-$]$_T$ concentration was set to 0.200 M and the [$Al(OH)_4^-$]$_T$ concentration was varied between 0.100 – 0.400 M.
During the deprotonation measurements the [Hpgl$^-$]$_T$ concentration was varied between 0.100 – 0.400 M, and the initial concentration of NaOH was 0.005 M. The titrant was 1.0114 M NaOH, with the ionic strength set to 4.0 M (NaCl).

Polarimetry
Polarimetric measurements have been performed using a Lippich-polarimeter equipped with LED light source, made by Krüss GmbH. The degrees of rotation (Θ) were measured on the wavelength of the sodium D line (590 nm) and the path length was 20 cm. The resolution of the instrument was 0.05°.

Computation
The equilibrium constants, the rotation and the molar rotation power of the species forming during the complexation of Hpgl$^-$ were calculated with the aid of the PSEQUAD suite of computer program [14]. The pK$_a$ values were calculated with the program pHCali v1.32a based on the nonlinear evaluation of the cell potential *vs.* titrant volume data [15].
The formation constants throughout this manuscript, β_{pq-r} are defined as:

$$\beta_{pq-r} = \frac{[A_p L_q H_{-r}^{p+q+r}]}{[A^-]^p [L^-]^q [H^+]^{-r}},$$

$$(2)$$

where A$^-$ and L$^-$ refer to: $Al(OH)_4^-$ and Hpgl$^-$, respectively.

RESULTS AND DISCUSSION

Potentiometric titrations

In order to determine the proton exchange processes of $Hpgl^-$, *i.e.* the deprotonation of OH group under alkaline conditions, potentiometric measurements were performed using H_2/Pt indicator electrode. The systematic positive shift of the cell potential with the increasing $[Hpgl^-]_T$ is caused by the deprotonation of the anion, forming $HpglH_{-1}^{2-}$ particles. From the shape of the curves only one deprotonation step was assumed. During the calculations, E^0 was held constant, and the ionic product of water (pK_w) was set to 14.26. The latter was determined earlier [16]. Fitting the four titration curves simultaneously the average difference of the measured and calculated EMF values was 0.31 mV, resulting to $logK_{01-1} = -13.88$ ± 0.002 (=0.38-14.26). This agrees well with the data found in the literature ($logK_{01-1} = -13.405 \pm 0.005$; $I = 1$ M NaCl) [17].
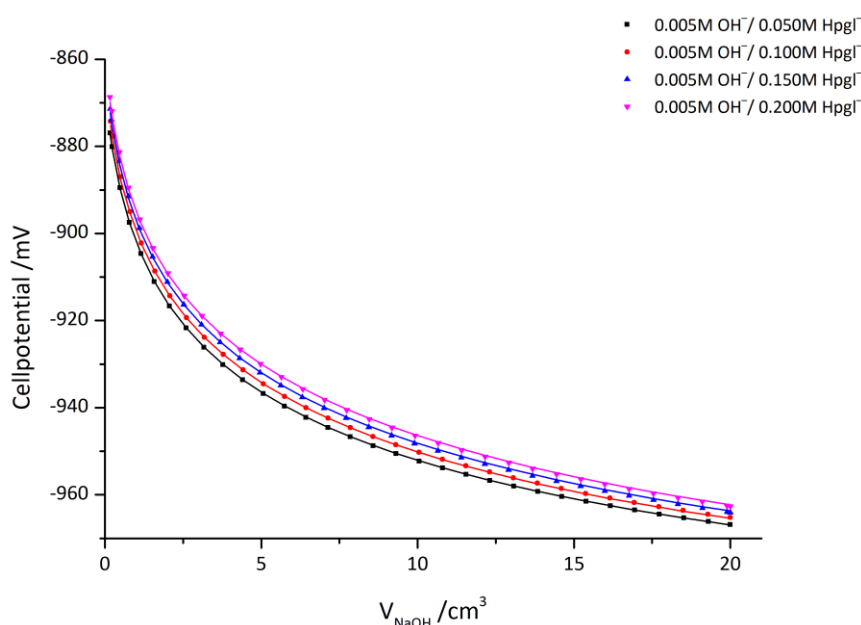

Figure 2: Potentiometric titration curves of the $H^+/Hpgl^-$ system. Symbols represent observed EMF values in the pH range of $12 - 13.6$ and the solid lines were fitted based on the model discussed in the text. $[NaOH]_0 = 0.005$ M, $I = 4.0$ M (NaCl). The titrant was 1.0114 M NaOH, with the ionic strength set to 4.0 M (NaCl)

To investigate the complexation of $Al(OH)_4^-$ with $Hpgl^-$, six titrations were performed with the platinized platinum electrode. During the evaluation of the titrations curves, the deprotonation constant was held constant at $logK_{01-1} = -13.88$. Similar to the deprotonation measurements, the curves shifted to higher EMF values upon increasing the ligand concentration. Observing the titration curves, notable changes in the curvature occurred only at 1:2 and 2:1 metal to ligand ration indicating the complex formation. In the first case, the end of the titration curve is in the slightly acidic pH region (pH = ~ 4), yet $Al(OH)_4^-$ did not formed $Al(OH)_3$ precipitate. Presumably, it was due to the well-buffered system, *i.e.* the complex formation, during the titration. Calculating the stability constants of the various species forming in the $Al(OH)_4^-/Hpgl^-$ system proved to be difficult due to the high correlation of the single species. Therefore, another individual method was needed to better understand the interactions in the system.
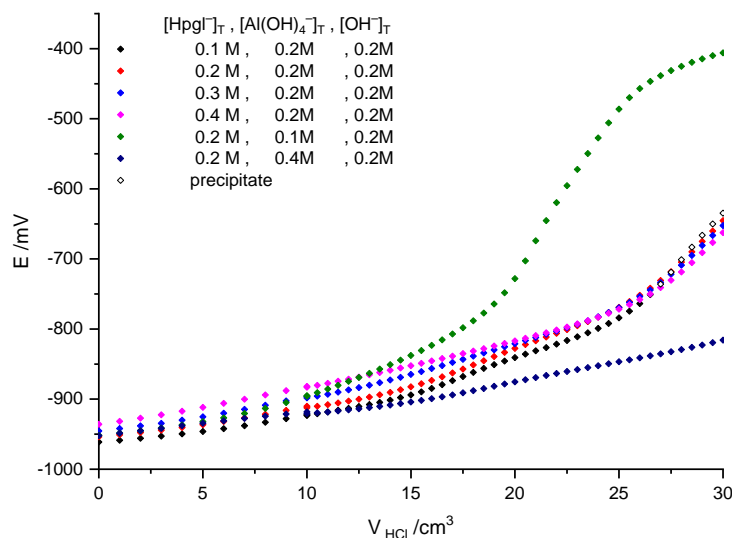
Figure 3: Potentiometric curves of the system containing $Al(OH)_4^-$ and $Hpgl^-$. The $[Hpgl^-]_T$ was varied from 0.100 to 0.400 M, the $[Al(OH)_4^-]_T$ and the $[OH^-]_T$ was held constant at 0.200 M. The titrant was 0.9889 M HCl, and the ionic strength was set to 4.0 M with NaCl.

Polarimetric measurements

Polarimetric measurements were performed in order to obtain the formation constants of the species with the compositions AL^{2-} and ALH^-, observed by Lakatos *et al.* in an earlier publication [17]. The solutions contained $[Hpgl^-]_T = [OH^-]_T = 0.200$ M in any case, the $[Al(OH)_4^-]_T$ was varied between 0 and 0.800 M and the ionic strength was set to 4.0 M NaCl. At first, the molar rotation of the ligand was measured. With the deprotonation constant of $logK_{01-1} = -13.88$, 95% of the ligand was in the form of $Hpgl^-$, so it was safe to assume, that $[Hpgl^-]_T \approx [Hpgl^-]$. The measured optical rotation was 0.4°, resulting in a molar rotation of 2°.

Observing the measured optical rotation, two possible models were assumed. In the first case, the formation of a simple 1:1 species with low stability constant was proposed. Alternatively, a polynuclear complex could be assumed, where the formation of the species took place in higher $Al(OH)_4^-$ concentrations. During the evaluation of the polarimetric measurements, the deprotonation constant of the ligand was held constant at $logK_{01-1} = -13.88$. Fitting the first model resulted $logK_{110} = 1.89 \pm 0.05$, with an average error in the observed rotation of 0.106°, and a calculated molar rotation of 31.51°. This constant agreed well with the value determined by Pallagi *et al.* earlier [18]. However, using this model, the deprotonated anion ($HpglH_{-1}^{2-}$) must have been included in the calculations, which species' molar rotation was undetermined. Calculating the molar rotation of the deprotonated anion resulted in 238.3°. Nevertheless, assuming a polynuclear complex, the linear combinations of the individual species were fitted with the same conditions, indicating a species with the stoichiometry of A_3L_2 with $logK_{320} = 5.23 \pm 0.12$. The average error between the measured and the calculated degrees of rotation was 0.103°, and the calculated molar rotation of the complex was 58.44°. During this calculation, the species $HpglH_{-1}^{2-}$ can be omitted from the fitting.
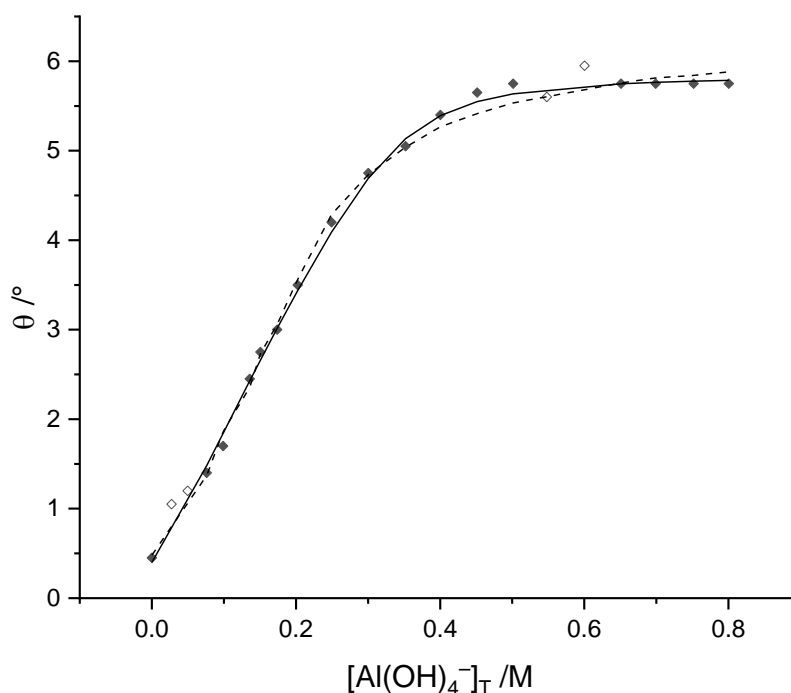
Figure 4: Observed (symbols) and calculated (lines, solid: 3:2 species, dashed: 1:1 species) optical rotation of the $Al(OH)_4^-/Hpgl^-$ system. $[Hpgl^-]_T$ and $[OH^-]_T$ was set to 0.200 M, and the $[Al(OH)_4^-]_T$ was varied from 0 to 0.800 M. The ionic strength was set to 4.0 M (NaCl).

CONCLUSIONS

The stability constant of the species forming in the $Al(OH)_4^-/Hpgl^-$ system was determined by polarimetric measurements. Two possible models were presumed, namely the 1:1 composition species, which was in a better agreement with the data found in the literature, and the 3:2 composition complex, which describes the observed changes better, but needs further validation by other methods. Considering, that in the case of calcium complexation, the ligands formed a chain-like structure where the metal fitted in between the individual sugar molecules, the formation of polynuclear complexes seems plausible also in the case of aluminum. For such studies, multinuclear (^{27}Al, ^{13}C, ^1H) NMR spectroscopy seems to be a method of choice, augmented by freezing point depression and ESI-MS spectroscopic measurements, for validating the model.

ACKNOWLEDGEMENTS

REFERENCES

[1] R.J. Motekaitis, A.E. Martell, Inorg. Chem. 23 (1984) 18.

[2] S. Giroux, S. Aury, B. Henry, P. Rubini, Eur. J. Inorg. Chem. (2002) 1162.

[3] X. Gaona, V. Montoya, E. Colàs, M. Grivé, L.Duro, Journal of Contaminant Hydrology102 (2008) 217.

[4] A. Venema, J. A.Peters, H. Van Bekkum, Recl. Trav. Chim., Pays−Bas 112 (1993) 445.

[5] S. Ramachandran, P. Fontanille, A. Pandey, C. Larroche, Food Technol. Biotech., 44, (2006), 185–195.

[6] C. Bube, V. Metz, E. Bohnert, K. Garbev, D. Schild, B. Kienzler, Phys. Chem. Earth, 64, (2013), 87–94.

[7] S. P. Rosenberg, D. J. Wilson, C. A. Heath, In Essential Readings in Light Metals, Vol. 1: Alumina and Bauxite, D. Donaldson, B. Raahauge, Eds., John Wiley & Sons, New York, NY, U.S., (2013), 210–216.

[8] A. Pallagi, Á. Gy. Tasi, G. Peintler, P. Forgó, I. Pálinkó, P. Sipos, Dalton. Trans., 42., (2013), 13470.

[9] T. Bechtold, E. Burtscher, A. Turcanu, J. Chem. Soc., Dalton. Trans., (2002), 2683–2688.

[10] B. Kutus, Cs. Dudás, G. Peintler, I. Pálinkó, P. Sipos, Carbohyd. Res., 460. (2018) 34-40.

[11] P. Sipos, G. Hefter , P. M. May, Analyst,125, (2000), 955.

[12] P. Sipos, G. Hefter and P. M. May, Aust. J. Chem.,51, (1998), 445.

[13] I. Kron, S. L. Marshall, P. M. May, G. Hefter,E. Königsberger, Monatshefte für Chemie,126, (1995), 819.

[14] L. Zékány I. Nagypál ,G. Peintler, PSEQUAD for Chemical Equilibria; Technical Software Distribution: Baltimore, MD, 1991.

[15] G. Peintler, B. Kormányos, B. Gyurcsik, pHCali v1.32a, 2007.

[16] Á. Buckó, B. Kutus, G. Peintler, I. Pálinkó, P. Sipos, Polyhedron 158 (2019) 117–124.

[17] A. Lakatos, T. Kiss, R. Bertani, A. Venzo, V. B. Di Marco, Polyhedron 27 (2008) 118–124.

[18] A. Pallagi, Z. Csendes, B. Kutus, E. Czeglédi, G. Peintler, P. Forgó, I. Pálinkó, P. Sipos, Dalton Trans., 42, (2013), 8460–8467.