

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

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Ph.D. Theses



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1. Introduction

Polyhydroxy carboxylates, such as gluconate (Gluc^-) play an essential role in a variety of industrial processing. Gluc^- is used in large quantities because of its complexing ability: for example NaGluc is a common additive in the construction industry and employed to improve certain properties of cement. In low- and intermediate-level (LL/IL) radioactive waste repositories, containers are filled with cement to prevent leakage, but upon water intrusion, the alkaline pore water might promote the complexation of metal ions by Gluc^- , therefore these complexing processes have been excessively studied in the past decades.

Gluc^- has been proven to be an efficient complexing agent for alkaline-earth (Ca(II) , Mg(II)) and transition (Cu(II) , Co(II) , Ni(II) , Mn(II) , Zn(II)) metal ions, therefore it cannot be disregarded that it might be capable of enhancing the solubility of tri- and tetravalent actinides and lanthanides in alkaline media. Anoxic conditions characteristic of radioactive waste repositories ensure that actinides are present in reduced oxidation states (Cm(III) , Am(III) , Pu(III) , Pu(IV)). Possible complexing agents are also present in these repositories such as organic ligands generated by the decomposition of contaminant cellulosic materials (isosaccharinate, Isa^-) or present as cement additives (Gluc^-).

It is of high priority to study the capability of these ligands to enhance the solubility of actinide ions in case of water intrusion, since the calculation of the degree of mobilization these metal ions can reach is integral for estimating the associated risk of disposal. Due to the pronounced chemical analogies, stable (III) oxidation state lanthanide ions share with trivalent actinides, tri- and tetravalent actinides can be modeled by less elaborate lanthanide ions. To obtain a simplified and relevant model of possible complexation processes in radioactive waste repositories, neodymium (Nd(III)) and Gluc^- have been employed previously as model ions in measurements carried out in aqueous solutions, but data acquired in alkaline equilibria are scarce.

2. Aims of the Thesis

Investigation of the binary $\text{Nd(III)}-\text{Gluc}^-$ system is necessary to assess the likelihood of Nd(III) forming polynuclear complexes. Collecting data in extreme conditions characteristic of storage sites (high ionic strength and pH) makes it possible to create more accurate models. Furthermore, the effect of large amounts of Ca(II) present in cement pore water has been scarcely investigated in regard to complexation equilibria, but published results trend towards Ca(II) promoting the formation of polynuclear complexes.

Considering these concerns, our first goal was to analyze the precipitates forming in binary Nd(III)–Gluc[−] and ternary Ca(II)–Nd(III)–Gluc[−] systems and to determine their composition and stoichiometry. We also aimed at creating models for the binary Nd(III)–Gluc[−] and ternary Ca(II)–Nd(III)–Gluc[−] aqueous systems accurately describing complexing reactions in the pH range 10–14 and to determine the stability constants of the complexes of the models. We investigated the coordination properties of Gluc[−] and how the binary and ternary complexes affect the solubility of Nd(III) when in contact with solid phase.

3. Experimental part

Precipitates of the Nd(III)–Gluc[−] and Ca(II)–Nd(III)–Gluc[−] systems were isolated and investigated via X-ray diffractometry, IR and DR spectroscopy. Morphologies of the precipitates were inspected via scanning electron microscopy while elemental analysis was carried out using energy dispersive X-ray spectroscopy (EDAX). Compositions were determined based on thermogravimetric and ICP-OES measurements.

Because of the appearing precipitate, reverse potentiometric titrations were carried out to quantify the complexation in binary Nd(III)–Gluc[−] and ternary Ca(II)–Nd(III)–Gluc[−] systems. Potentiometric curves were fitted simultaneously with acquired spectrophotometric data using PSEQUAD in case of both systems. For the binary samples assuming the formation of only mononuclear complexes was not sufficient to reproduce the collected data, and inclusion of binuclear complexes in the chemical model was necessary. Freezing point depression, CD and NMR measurements were applied to validate the model. For the ternary solutions simultaneous evaluation of potentiometric and spectrophotometric data resulted in a model consisting of three polynuclear complexes. NMR and CD results validate complex formation. The created models were utilized to carry out a simulation assuming conditions characteristic of radioactive repositories to inspect how the solubility of Nd(III) is affected. Coordinating properties of Gluc[−] were also investigated via CD and NMR measurements and other ligands such as gulonate and galactonate were also studied for comparison via the same methods.

4. New scientific results

T1. We have isolated solid complexes precipitating from Nd(III)–Gluc[−] and Ca(II)–Nd(III)–Gluc[−] solutions, determined their composition and shown a correlation between the stoichiometries of solid complexes and complexes in solution in the case of the binary system.

The composition of the complexes: $\text{NdGlucH}_{-1}(\text{OH})\cdot 2\text{H}_2\text{O}$



The composition was determined by thermogravimetric (crystalline water) and ICP-OES (Ca(II):Nd(III) ratio) measurements. The FT-IR spectra demonstrated that both complexes contain Gluc[−] and indicate bidentate coordination of the carboxylate functional group, while the similarity of the DR spectra is due to the invariance of the coordination environment of Nd(III).

T2. It has been experimentally demonstrated that Nd(III) can form binuclear complexes in the presence of Gluc[−] ions in the pH > 10 range. We have successfully determined the composition and stability constant of the complexes formed in the Nd(III)–Gluc[−] system in strongly alkaline media.

Matrix rank analysis was performed on the spectrophotometric data set, which suggested the presence of at least three colored particles in the binary system. By fitting the potentiometric and spectrophotometric data together, a model was constructed that reproduces the experimental data well. The chosen model was supported by freezing point depression measurements.

T3. We found that the metal-ligand interaction is the strongest for complexes formed in neutral solutions and weakens with increasing pH. The biner Nd(III)–Gluc[−] complexes formed were compared with Nd(III) complexes of galactonate and gulonate and the functional groups involved in the coordination of Nd(III) were suggested.

By comparing the NMR and CD spectra of Nd(III)-gluconate, -gulonate and -galactonate complexes, it can be stated that at high pH ranges, hydroxyl functions other than the α -hydroxyl group, at positions distant from the carboxylate, are involved in the coordination. Of these, the involvement of hydroxyl groups at the β - and δ -positions is most likely.

T4. We have demonstrated the formation of ternary complexes in Ca(II)–Nd(III)–Gluc[−] systems in strongly alkaline solutions and found that they are characterized by a uniform Ca(II):Nd(III) = 3:1 ratio. We determined the composition and stability factor of the formed ternary complexes.

Using matrix rank analysis, the number of complexes formed in the highly alkaline range of the ternary system was determined. By fitting the potentiometric and spectrophotometric data together, a model was constructed which simulates the measured data series well.

T5. We have confirmed that hydroxyl groups involved in the coordination play an important role in the formation of ternary complexes. We have shown that Ca(II) ions induce a change in the conformation of gluconate.

A new peak in the ¹H spectra of ternary solutions provides further evidence for the formation of ternary complexes: it suggests that there is slow exchange between free ligand and complexes, which suggests strong metal-ligand interaction. The difference between the CD spectra of the binary Nd(III)–Gluc[−] and ternary Ca(II)–Nd(III)–Gluc[−] solutions indicates a change in the conformation of Gluc[−].

T6. Simulations under conditions typical of radioactive repositories suggest that neither the formation of binary nor ternary complexes contributes significantly to the increase in solubility of lanthanide ions.

The high Ca(II) concentrations typical of radioactive repositories ensure that Gluc[−] is in solution in the form of Ca(II)–Gluc[−] complexes, thus precluding the possibility that binary Nd(III)–Gluc[−] or ternary Ca(II)–Nd(III)–Gluc[−] complexes further increase the solubility of Nd(III).

5. Practical applications

As highlighted previously, our final goal was to provide a comprehensive overview of a complex three-component equilibrium system, which can provide an accurate description of alkaline equilibria present in cementitious radioactive repositories. Models developed for binary Nd(III)–Gluc[−] and ternary Ca(II)–Nd(III)–Gluc[−] systems contribute to a better understanding of the complexation reactions taking place in aqueous equilibria of radioactive storage sites and enables quantitative evaluation of associated risk upon water intrusion. Elaborate study of the structure of forming complexes may provide new insights into the overall complexing ability of Gluc[−].

6. Publications and conference participations

6.1. Full papers directly related to the Thesis published in peer-reviewed journals

1. **É. Böszörményi**, J. Lado- Sanjurjo, Cs. Dudás, B. Kutus, M. Szabados, G. Varga, I. Pálinkó, P. Sipos: The structure and composition of solid complexes comprising of Nd(III), Ca(II) and D-gluconate isolated from solutions relevant to radioactive waste disposal, Pure and Applied Chemistry, vol. 92(10), 2020, 1709-1715.
<https://doi.org/10.1515/pac-2019-1010>, **Impact factor (2020): 2.453**

2. **É. Böszörményi**, Zs. Kása, G. Varga, Z. Kele, B. Kutus, G. Peintler, I. Pálinkó, P. Sipos: Formation of mono- and binuclear complexes of Nd³⁺ with D-gluconate ions in hyperalkaline solutions – Composition, equilibria and structure, Journal of Molecular Liquids, vol. 346, 2022, 117047.
<https://doi.org/10.1016/j.molliq.2021.117047>, **Impact factor (2022): 6.165**

3. **É. Böszörményi**, O. Dömötör, B. Kutus, G. Varga, G. Peintler, P. Sipos: Coordination motifs of binary neodymium(III) D-gluconate, D-galactonate and L-gulonate complexes and the transition from inner- to outer-sphere coordination in neutral to strongly alkaline medium, Journal of Molecular Structure, vol. 1261, 2022, 132894.
<https://doi.org/10.1016/j.molstruc.2022.132894>, **Impact factor (2022): 3.196**

6.2. Full papers directly related to the Thesis published in conference proceedings

1. **É. Böszörményi**, J. Lado-Sanjurjo, M. Szabados, G. Varga, I. Pálinkó, P. Sipos: The structure and composition of solid complex compounds precipitating from binary Nd(III)–gluconate and ternary Ca(II)–Nd(III)–gluconate solutions, XXVII. ICCBIC June 2 – 7, 2019, Smolenice, Slovakia

2. **É. Böszörményi**, O. Dömötör, G. Varga, G. Peintler, P. Sipos, B. Kutus: Formation of heteronuclear complexes in the ternary Ca²⁺ – Nd³⁺ – Gluc⁻ system XXVIII. ICCBIC, June 5 – 10, 2022, Smolenice, Slovakia

3. **É. Böszörményi**, Zs. Kása, G. Peintler, I. Pálinkó, P. Sipos: Egyensúlyok biner neodímium–glükonát és terner kalcium–neodímium–glükonát rendszerek vizes oldataiban, 54. Komplexkémiái Kollokvium, 2021. May 26-27, On-line

4. **É. Böszörményi**, B. Kutus, O. Dömötör, G. Peintler, P. Sipos:

Terner kalcium – neodímium – glükonát rendszert leíró kémiai modell meghatározása,

55. Komplexkémiái Kollokvium, 2022. May 25-27. Debrecen

5. B. Kutus, **É. Böszörményi**, G. Peintler, P. Sipos:

Komplekképződés neodímium-, kalcium- és glükonátionokat tartalmazó vizes oldatokban, pH = 2 és 14 között,

55. Komplexkémiái Kollokvium, 2022. May 25-27. Debrecen

6.3. Full papers not directly related to the Thesis published in peer-reviewed journal

1. Cs. Dudás, B. Kutus, **É. Böszörményi**, G. Peintler, Z. Kele, I. Pálinkó, P. Sipos:

Comparison of the Ca²⁺ complexing properties of isosaccharinate and gluconate – is gluconate a reliable structural and functional model of isosaccharinate?

Dalton Transactions, vol. 46, 2017, 13888

<https://doi.org/10.1039/c7dt03120c>, **Impact factor (2017): 4.160**

2. Cs. Dudás, B. Kutus, **É. Böszörményi**, G. Peintler, Amr A. A. Attia, A. Lupan, Z. Kele, P. Sipos, I. Pálinkó: Calcium complexing behaviour of lactate in neutral to highly alkaline medium, Journal of Molecular Structure, vol. 1180, 2019, 491-498.

<https://doi.org/10.1016/j.molstruc.2018.12.020>, **Impact factor (2019): 2.463**

3. R. Mészáros, S. Ötvös, G. Varga, **É. Böszörményi**, M. Kocsis, K. Karádi, Z. Kónya, A. Kukovecz, I. Pálinkó, F. Fülöp: A mineralogically-inspired silver–bismuth hybrid material: Structure, stability and application for catalytic benzyl alcohol dehydrogenations under continuous flow conditions, Molecular Catalysis

Vol. 498, 2020, 111263.

<https://doi.org/10.1016/j.mcat.2020.111263>, **Impact factor (2020): 5.062**

6.4. Other full papers not directly related to the Theses published in conference proceedings

1. Cs. Dudás, B. Kutus, **É. Böszörményi**, P. Medvegy, O. Orbán-Gyapai, I. Pálinkó, P. Sipos:

Kalcium- és nátrium-izoszacharinát előállítása és jellemzése

XXXVIII. Kémiai Előadói Napok, Szeged, 2015 ISBN 978-963-9970-64-9, pp. 42–47

2. **É. Böszörményi**, Cs. Dudás, B. Kutus, I. Pálinkó, P. Sipos:

Az izoszacharinát- és a glükonát-ion sav-bázis és kalcium-komplekképző tulajdonságainak összehasonlítása

XXXIX. Kémiai Előadói Napok, Szeged, 2016, ISBN 978-963-9970-73-1, pp. 60–64.

3. Cs. Dudás, **É. Böszörményi**, B. Kutus, I. Pálinkó, P. Sipos Pál:

Az izoszacharinát ion sav-bázis és kalcium-komplekképző sajátságai semleges és lúgos oldatokban

50. Komplexkémiai Kollokvium, 2016. május 30.-június 1., Balatonvilágos

4. **É. Böszörményi**, Cs. Dudás, B. Kutus, I. Pálinkó, P. Sipos:

Az izoszacharinát és laktát ionok semleges és lúgos kémhatású oldatokban képződő kalciumkomplexeinek összehasonlítása,

XL. Kémiai Előadói Napok, Szeged, Magyarország, 2017. október 16-18.

5. Cs. Dudás, **É. Böszörményi**, B. Kutus, I. Pálinkó, P. Sipos:

Comparison of the deprotonation and calcium complexation of isosaccharinate and gluconate ions in highly alkaline solutions,

33rd European Congress on Molecular Spectroscopy, Szeged, Magyarország, 2016. július 30.-augusztus 4.

6. Cs. Dudás, **É. Böszörményi**, B. Kutus, I. Pálinkó, P. Sipos:

Comparison of the Behavior of Isosaccharinate and Gluconate Ions in the Presence of Calcium, International Congress of Young Chemists, Czestochowa, Lengyelország, 2016. október 5-9.

7. Cs. Dudás, **É. Böszörményi**, B. Kutus, I. Pálinkó, P. Sipos:

Calcium Complexing Properties of Isosaccharinate Ion in Highly Alkaline Environment, 19. World academy of science, engineering and technology, Párizs, Franciaország, 2017. március 29-30

8. B. Kutus, Cs. Dudás, A. Gácsi, Á. Buckó, Sz. Ziegenheim, **É. Böszörményi**, T. Faragó, G. Peintler, I. Pálinkó, P. Sipos:

Calcium complexation processes in hyperalkaline aqueous solutions

XXVI ICCBIC, June 4 – 9, 2017, Smolenice, Slovakia

9. **É. Böszörményi**, Á. Buckó, G. Peintler, P. Sipos, B. Kutus:

Progress in the aquatic chemistry of heteropolynuclear complexes of polyhydroxy carboxylates, XXVIII ICCBIC, June 5 – 10, 2022, Smolenice, Slovakia

