Radiochim. Acta **91**, 599–602 (2003)

Complex formation of Tb^{3+} with glycolate, *D*-gluconate and α-isosaccharinate in neutral aqueous perchlorate solutions

By K. P. Zhernosekov[1], E. Mauerhofer[1], G. Getahun[1], P. Warwick[2] and F. Rösch[1,*]

[1] Institut für Kernchemie, Johannes Gutenberg-Universität, D-55128 Mainz, Germany
[2] Centre for Environmental Studies, Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

(Received January 30, 2003; accepted in final form May 23, 2003)

Electromigration / Stability constants / Glycolate / D-gluconate / α-Isosaccharinate / Ion mobility

Summary. An electromigration technique was used for measurements of metal-ligand formation constants of non-carrier-free $^{160}Tb^{3+}$ with glycolate, *D*-gluconate and α-isosaccharinate ligands. The overall ion mobilities of Tb at different concentrations of the ligands were measured in chemically inert perchlorate solutions (pH 7 and $T = 298.1$ K) with an overall ionic strength $\mu = 0.1$. The stepwise stoichiometric stability constants are: Tb^{3+}/glycolate: $\log K_1 = 2.72(18)$, $\log K_2 = 1.73(19)$, $\log K_3 = 1.12(17)$, Tb^{3+}/*D*-gluconate: $\log K_1 = 2.96(11)$, $\log K_2 = 2.60(11)$, $\log K_3 = 1.13(9)$, Tb^{3+}/α-ISA: $\log K_1 = 3.07(8)$, $\log K_2 = 2.69(11)$, $\log K_3 = 1.80(12)$.

Introduction

One possibility of disposal of low- and intermediate-level radioactive waste is deposition in a deep underground repository. When full, the repository may be backfilled with cement (NIREX Reference Vault Backfill, NRVB) [1]. After closure, the repository will become saturated with groundwater, and highly alkaline porewater (pH about 13) will be produced because of dissolution of the cement. The porewater is also expected to be anaerobic because of steel canister corrosion. Wastes will contain cellulose from paper, cloth and wood and this will degrade under the high pH conditions of the repository. Under alkaline, anaerobic conditions at temperatures below 170 °C (*i.e.* the likely conditions in the near-field), the main degradation mechanism entails a beta-alkoxycarbonyl elimination, which ruptures the 1,4-glycosidic linkage and takes place at the reducing group at the end of the chain (peeling reaction). The erythro and threo isomers of 2-C-(hydroxymethyl)-3-deoxy-D-pentonic acid (isosaccharinic acid, ISA) are important degradation products [2–5]. Under alkaline conditions, deprotonation of the hydroxyl groups is expected [5–10], resulting in chelation and larger formation constants. Therefore, measurements of those formation constants are of interest when considering the performance assessment of a repository.

The measurements reported here were performed at pH = 7.00(5), where relatively weak salt formation is expected. However, measurements at pH 7 are important because of a lowering of pH occurring by dilution of the near-field porewaters by far-field groundwaters. Furthermore, under highly alkaline condition, hydrolysis of radiometals and complex formation overlap. For understanding the complex formation processes under highly alkaline condition, comparative data on the processes of complexation in neutral system are essential. Thus, the present work might serve as a quantitative input for studies to be conducted subsequently at pH $\geqq$ 12.

In addition to α-ISA, *D*-gluconate and glucolate were investigated. Gluconic acid as well as α-ISA belongs to the polyhydroxy ligands [8] and is the close structure analogue of α-ISA. Its complexation reactions are of interest to understand ligand structure-complex formation relationships. Glycolic acid having only one hydroxyl group has been investigated in order to determine the effect of chain length on the formation constants.

In this study, ^{160}Tb was used as a model radioisotope, with Tb(III) representing the trivalent elements of the $4f$ and $5f$ groups. The isotope ^{160}Tb emits photon radiation useful for the on-line migration detection and can be produced in high specific activity. The electromigration technique, in contrast to several other analytical techniques, is capable of measuring complex formation processes of radiometals at ultra-low, even no-carrier-added concentration and is therefore of considerable significance, considering the low concentration of radioactive metals present in those systems.

Experiments and methods

^{160}Tb ($T_{1/2} = 72.3$ d) was produced by neutron irradiation of 5 mg of terbium oxide at the BERII reactor (HMI, Berlin). The specific activity of $^{160}Tb_2O_3$ was about 470 MBq mg^{-1} at the end of the irradiation. A stock solution of Tb was prepared by dissolving the oxide in 0.1 M HNO_3. Experimental solutions for electromigration measurements were prepared by (i) evaporating 200 μL of the ^{160}Tb stock solution of 30 MBq/mL specific activity in 0.1 M HNO_3 to dryness and (ii) dissolving the residue in 100 μL $NaClO_4$, pH ≈ 4. About 1–2 μL of the ^{160}Tb solution, *i.e.* approximately 10^{-8} mol of Tb^{3+}, were in-

*Author for correspondence (E-mail: frank.roesch@uni-mainz.de).

jected into the electromigration tube, which contains the electrolyte.

Aqueous solutions of the type $NaL/NaClO_4$ or $HL/NaClO_4$ were used in the investigations. NaL represents the sodium salt of α-ISA (Na-ISA) whereas HL represents the glycolic and *D*-gluconic acids, respectively. The concentration range was 10^{-8}–10^{-1} M for the glycolic and *D*-gluconic acids, and 10^{-7}–10^{-2} M for Na-ISA. Appropriate amounts of NaOH were added to the solutions to adjust their pH to 7.00(5), while maintaining a constant overall ionic strength of $\mu = 0.1$. At pH ≈ 7 the carboxylic functional groups of the glycolic and *D*-gluconic acids are deprotonated (pK_s constants are 4.76 and 3.7, respectively) and the concentration of the ligands is equal to the concentration of the acids.

The *D*-gluconic and the glycolic acids were analytical grade chemicals purchased from Fluka. $Ca(\alpha\text{-ISA})_2$ was synthesized according to the procedure reported by Whistler *et al.* [11]. The sodium salt of α-ISA was prepared by passing $Ca(\alpha\text{-ISA})_2$ through a cation exchange column (Chelex-100 resin, BioRad) in the Na^+-form [12]. The absence of Ca^{2+} has been assessed applying Atomic Absorption Spectroscopy. The amount of Ca^{2+}-ions was found to be 56(17) μg in 1 g of Na(α-ISA).

The inert background electrolytes $NaOH/NaClO_4$ were prepared using p.a. chemicals. To prepare the solutions analytical grade water was used. The pH of the electrolytes was measured by means of pre-calibrated glass electrode using standard buffer solutions.

The overall ion mobilities were measured by means of free-electrolyte continuous electromigration technique at $T = 298.1(1)$ K and setting an electric field intensity of 10 V/cm. The apparatus and the analytical procedure used in this work for the on-line determination of absolute migration velocities of radio-ions are described in detail elsewhere [13, 14]. To avoid electro-osmosis and wall sorption, the inner surface of the migration glass tube was coated with monomolecular layer of non-cross-linked polyacrilamide according to the method reported by Hjertén [15].

Each value of the overall ion mobility reported is an average of two to four independent measurements with a precision ranging between 0.5 and 2%. The standard deviation on the average value of the absolute ion mobility ranges from 2 to 3%.

Results and discussion

General treatment

The quantitative treatment of the experimental data of the overall ion mobility is based on mechanism (1), which is generally accepted for the interpretation of metal-ligand (M^{n+}-L^-) interactions:

$$ML_{m-1}{}^{(n-m+1)} + L^- \overset{K_m}{\longleftrightarrow} ML_m{}^{(n-m)}\,, \qquad (1)$$

where K_m ($m \geq 1$) are the stepwise stoichiometric complex formation constants.

The overall stoichiometric complex formation constant is

$$\beta_m = \prod K_m\,. \qquad (2)$$

The hydrolysis of M^{n+} can be expressed as:

$$M(OH)_{a-1}{}^{(n-a+1)+} + H_2O \overset{K_a^{hyd}}{\longleftrightarrow} M(OH)_a{}^{(n-a)+} + H^+\,, \qquad (3)$$

where K_a^{hyd} ($a \geq 1$) are the stepwise stoichiometric constants for a hydrolysis product.

The overall ion mobility of the metal in the presence of a complex forming agent L^- can be calculated as the sum of the absolute individual ion mobilities of the species $ML_m{}^{(n-m)+}$ weighted with their relative concentration [16–18] as

$$u = \sum u^\circ_{ML_m{}^{(n-m)}} \frac{[ML_m{}^{(n-m)}]}{[M]_{total}}\,. \qquad (4)$$

Substituting the stepwise complex formation constants K_m and K_a^{hyd} in the above equation, the overall ion mobility of the radiometal may be expressed as a function of the ligand concentration as follows:

$$u = \frac{\left\{\begin{array}{l} u^\circ_{M^{n+}} + \sum u^\circ_{ML_m{}^{(n-m)}} [L^-]^m \prod K_m \\ + \sum u^\circ_{M(OH)_a{}^{(n-a)}} [H^+]^{-a} \prod K_a^{hyd} \end{array}\right\}}{1 + \sum [L^-]^m \prod K_m + \sum [H^+]^{-a} \prod K_a^{hyd}}\,. \qquad (5)$$

The absolute individual ion mobility of the species $ML_m{}^{(n-m)}$ and $M(OH)_a{}^{(n-a)}$ can be derived from the correlation observed between the ionic charge and the individual ion mobility of the species independent of the type of ligand [17, 18]:

$$\frac{u^\circ_{M^{n+}}}{u^\circ_{ML_m{}^{(n-m)+}}} = \frac{+n}{+(n-m)}\,. \qquad (6)$$

The $u^\circ_{M^{n+}}$-value can be obtained from the experimental data in the absence of ligands, *i.e.* when M^{n+} and $M(OH)_a{}^{(n-a)}$ are the only species present in the electrolyte according to Eqs. (5), (6), and the stepwise formation constants for hydrolysis products are known.

The values of K_m could be obtained after considering the influence of Tb(III) hydrolysis on the absolute ion mobility by fitting the experimental data $u = f([L^-])$ with Eq. (5).

Complex formation of $^{160}Tb^{3+}$

The experimental results on the overall ion mobility obtained for $^{160}Tb^{3+}$ species in $NaClO_4$ background electrolytes with various concentrations of glycolate, *D*-gluconate and α-isosaccharinate are shown in Figs. 1, 2 and 3, respectively. The described treatment of the overall ion mobility was applied to Tb^{3+} with $m = 1$, 2, 3 and limiting the hydrolysis to its first step ($a = 1$), which is reasonable at pH = 7.00(5). At infinite dilution ($\mu = 0$), $\log K_1^{hyd}$ is -7.90 and for perchlorate medium ($\mu = 0.1$), $\log K_1^{hyd}$ is -8.27 [19].

The absolute individual ion mobilities of the Tb^{3+} species obtained for each complexation are listed in Table 1. The stepwise formation constants K_m obtained from the fit of the experimental data with Eq. (5) (solid lines in Figs. 1, 2 and 3) are given in Table 2. Mathematical fitting is sensitive as evidenced by the given statistical errors. Relative differences between the ligands are thus reliable, although the stepwise stability constants do not differ significantly in their absolute values.

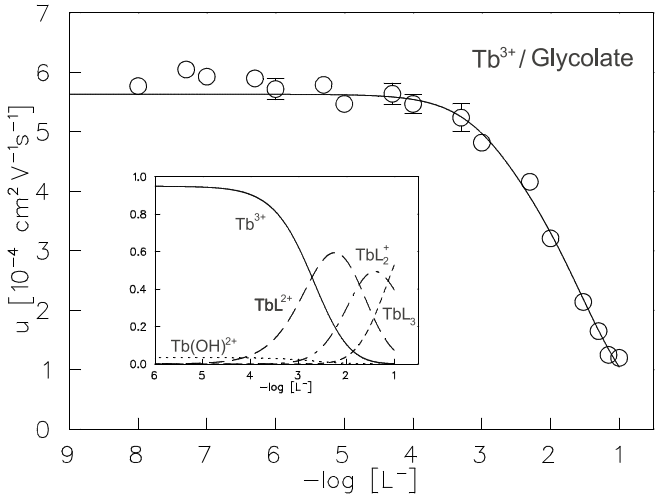

Fig. 1. Overall ion mobility of $^{160}Tb^{3+}$ species *versus* glycolate ligand concentration. HL/NaOH/$NaClO_4$ electrolytes, $T = 298.1(1)$, pH = 7.00(5), $\mu = 0.1$. The window in the plot shows the relative distribution of the species.

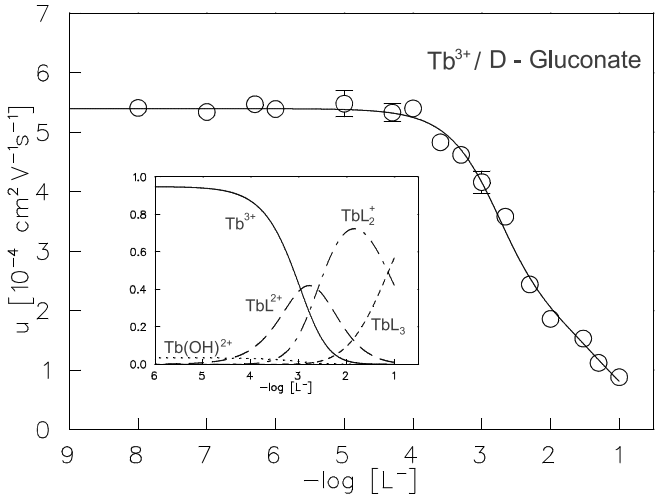

Fig. 2. Overall ion mobility of $^{160}Tb^{3+}$ species *versus* *D*-gluconate ligand concentration. HL/NaOH/$NaClO_4$ electrolytes, $T = 298.1(1)$, pH 7.00(5), $\mu = 0.1$. The window in the plot shows the relative distribution of the species.

Speciation was calculated according to the mole fractions of the species and the stepwise formation equilibria. The windows in the Figs. 1, 2 and 3 show the relative distribution of the species.

The values for complexation of terbium with glycolate and *D*-gluconate are close to literature values [20].

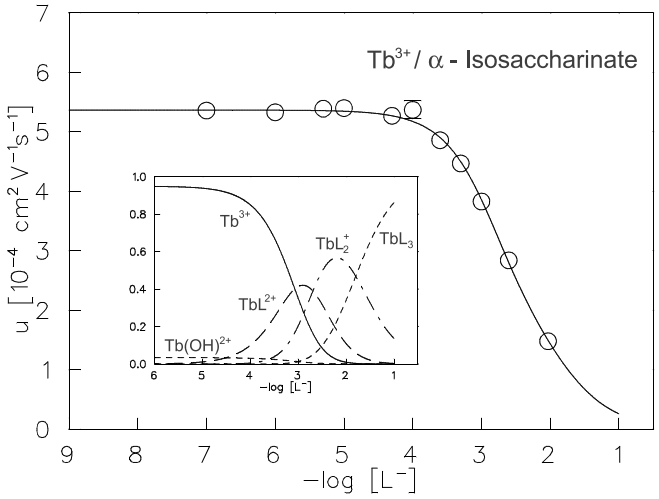

Fig. 3. Overall ion mobility of $^{160}Tb^{3+}$ species versus α-isosaccharinate ligand concentration. NaL/NaOH/$NaClO_4$ electrolytes, $T = 298.1(1)$, pH 7.00(5), $\mu = 0.1$. The window in the plot shows the relative distribution of the species.

Table 1. Absolute individual ion mobility u_i° (10^{-4} cm^2 V^{-1} s^{-1}) of the species for the complex formation of terbium with glycolate, *D*-gluconate and α-isosaccharinate ligands. Background electrolyte: Na(OH)ClO_4, $\mu = 0.1$, pH = 7.00(5), $T = 298.1(1)$ K.

Ligand	$u_{Tb^{3+}}$ [a]	$u^\circ_{Tb^{3+}}$	$u^\circ_{Tb(OH)^{2+}}$	$u^\circ_{TbL^{2+}}$	$u^\circ_{TbL_2^+}$
Glycolate	5.63(16)	5.73(16)	3.82(11)	3.82(11)	1.91(5)
D-gluconate	5.40(6)	5.49(6)	3.66(4)	3.66(4)	1.83(2)
α-Isosaccharinate	5.37(11)	5.46(11)	3.64(2)	3.64(2)	1.82(1)

a: overall ion mobility of Tb^{3+} species in Na(OH)ClO_4 free from ligand.

For the investigated ligands, trivalent metal cations such as Tb^{3+} form complexes whose stability, in particular if expressed *via* the overall stability constants $\log \beta_3$, increases in the order glycolate < *D*-gluconate < α-isosaccharinate. At 0.1 M ligand concentration, the main species are TbL_2^+ and TbL_3 for complexation with glycolate and *D*-gluconate, while for complexation with α-isosaccharinate the main species is TbL_3 (see windows in Figs. 1, 2 and 3). The hydrolysis product $Tb(OH)^{2+}$ disappears at a ligand concentration higher than 10^{-3} M.

Conclusion

Values of the formation constants for the reactions of Tb^{3+} with glycolate, *D*-gluconate and α-isosaccharinate in neutral perchlorate solutions at $T = 298.1(1)$ K, pH = 7.00(5)

Table 2. Stepwise complex formation constants ($\log K_m$) for the complexation of terbium with glycolate, *D*-gluconate and α-isosaccharinate ligands. $\log \beta_3$ is the overall complex formation constant. Background electrolyte: Na(OH)ClO_4, $\mu = 0.1$, pH = 7.00(5), $T = 298.1(1)$ K.

Ligand	$\log K_1$	$\log K_2$	$\log K_3$	$\log \beta_3$	Ref.
Glycolate	2.72(18)	1.73(19)	1.12(17)	5.57(54)	This work
	2.82[a]	2.09[a]	1.12[a]	6.03[a]	[20]
D-gluconate	2.96(11)	2.60(11)	1.13(9)	6.69(31)	This work
	2.47[b]	2.20[b]	1.11(9)[b]	–	[20]
α-Isosaccharinate	3.07(8)	2.69(11)	1.80(12)	7.56(31)	This work

a: $\mu = 0.1$;
b: $\mu = 0.2$.

and $\mu = 0.1$ have been evaluated by measuring the overall ion mobility of the complexes using the free electrolyte electromigration technique. Complexation formation constants of terbium with glycolate and *D*-gluconate are close to literature values. Tb^{3+} as a model element for trivalent lanthanides and actinides forms complexes whose stability, in particular if expressed *via* the overall stability constants $\log \beta_3$, increases in the order glycolate $<$ *D*-gluconate $<$ α-isosaccharinate. However, gluconic acid and α-ISA as close structure analogues thus form complexes of not very different stability. Glycolic acid, having one hydroxyl group less, shows a lower tendency for complex formation.

The absolute individual ion mobilities of TbL_m^{3-m}-complexes as well as those involved in hydrolysis formation have been identified. A knowledge of these characteristics is a prerequisite for subsequent investigation of relevant equilibria in alkaline solution. In this context the presented method is useful to study the complex formation occurring parallel to secondary processes such as hydrolysis of cations. Further measurements will be made at high pH (12–13) in order to investigate the expected stronger complexes.

Acknowledgment. The financial support by the Deutsche Forschungsgemeinschaft (DFG Ro 985/7-3) is gratefully acknowledged. The authors would like to thank the colleagues at the BER II reactor for the irradiations.

References

1. Proceedings of the Royal Society of Chemistry/NIREX Symposium. The Chemistry of Deep Disposal of Radioactive Waste, Loughborough University, December 10 (1997) (Available from UK NIREX).
2. Greenfield, B. F., Hurdus, M. H., Pilkington, N. J., Spindler, M. W., Williams, S. J.: The degradation of cellulose in the near field of a radioactive waste repository. Materials Research Society Symposium Proceedings, 333, Scientific Basis for Nuclear Waste Management XV11, Materials Research Society (1994).
3. Greenfield, B. F., Harrison, W. N., Robertson, G. P., Somers, P. J., Spindler, M. W.: Mechanistic Studies of The Alkaline Degradation of Cellulose in Cement. Safety Studies Nirex Radioactive Waste Disposal. AEA Technology, Harwell (1993).
4. Greenfield, B. F., Holtom, G. F., Hurdus, M. H., O'Kelly, N., Pilkington, N. J., Rosevear, A., Spindler, M. W., Williams, S. J.: Mat. Res. Soc. Symp. Proc. **353**, 1151 (1995).
5. Dimmock, P. W., Warwick, P., Robbins, R. A.: Analyst **120**, 2159 (1995).
6. Van Duin, M., Peters, J. A., van Bekkum, H. A.: Recl. Trav. Chim. Pays-Bas **108**, 57 (1989).
7. Van Loon, L. R., Glaus, M. A., Laube A., Stallone S.: Radiochim. Acta **86**, 183 (1999).
8. Sawyer, D.: Chem. Rev. **64**, 633 (1964).
9. Vercammen, K., Glaus, M. A., Van Loon, L. R.: Acta Chem. Scandinavica **53**, 246 (1999).
10. Vercammen, K., Glaus, M. A., Van Loon, L. R.: Radiochim. Acta **84**, 221 (1999).
11. Whistler, R. L., BeMiller, J. N.: Methods Carbohydrate Chem. **2**, 477 (1963).
12. Glaus, M. A., Van Loon, L. R., Achatz, S., Chodura, A., Fischer, K.: Anal. Chim. Acta **398**, 111 (1999).
13. Mauerhofer, E., Rösch, F.: Radiochim. Acta **89**, 537 (2001).
14. Mauerhofer, E., Kling, O., Rösch, F.: Radiochim. Acta **88**, 399 (2000).
15. Hjertén, S. J.: Chromatogr. **347**, 191 (1985).
16. Lundqvist, R.: Acta Chem. Scand. A **35**, 31 (1981).
17. Dmitriev, S. N., Milanov, M. V., Maslov, O. D.: Radiochemistry **42**, 103 (2000).
18. Rösch, F., Khalkin, V. A., Milanov, M., Hung, T. K.: Z. Chem. **10**, 358 (1987).
19. Baes, C., F., Mesmer, R. E.: *The Hydrolysis of Cations*. Krieger Publisher Company, Inc., Florida. (1986).
20. Martell, A. E., Smith, R. M.: *Critical Stability Constants*. Vol. 3, Plenum New York and London (1997).