Complex formation of $^{160}Tb^{3+}$ with α-isosaccharinate in inert electrolytes

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In the deep underground repository of low and intermediate-level radioactive wastes the α-isosaccharinic (α-ISA) acid may be among the alkaline degradation products of the cellulose present in the waste [1]. The complexation of such ligands with metal ions is highly essential to investigate solubility, sorption and migration of radionuclides in near and far fields of radioactive waste disposal. However, α-ISA is difficult to produce and gluconic acid may be evaluated as an analogue of α-ISA.

Complex formation equilibria of Tb^{3+} with α-isosaccharinate ligand in neutral aqueous electrolytes (pH = 7) at T = 298.1 K were investigated by means of electromigration measurements of non-carrier-free $^{160}Tb^{3+}$.

^{160}Tb ($T_{1/2}$ = 72.3 d) was produced by neutron irradiation of terbium oxide at the BER II reactor (HMI, Berlin). Terbium solutions for electromigration measurements were prepared by evaporation of about 200 μL of a $^{160}Tb^{3+}$ - stock solution and dissolution of the residue with 100 μL of $Na(H)ClO_4$, pH = 4.

Aqueous solutions of type $NaClO_4$/NaOH/HL with an overall ionic strength μ = 0.1 and a pH = 7.0(1) were used for the investigations, L = ligand. The sodium salt of α-ISA (Na-ISA) was synthesized via the procedure described elsewhere [2]

The pH of the electrolytes was measured by means of glass electrodes calibrated by standard buffer solutions.

The volume of the $^{160}Tb^{3+}$ solutions injected into the electrolyte in the electromigration tube was about 1-2 μL corresponding to a metal amount in the migration zone of ≈ 10^{-7}. Measurements of absolute ion mobilities were performed with an electric field intensity of 10 V/cm.

The experimental results obtained for the $^{160}Tb^{3+}$/α-isosaccharinate system are illustrated in Fig.1.

The quantitative treatment of the experimental results was based on the following mechanism (Eq.1):

$$ML_{m-1}^{(n-m+1)+} + L^- \xleftrightarrow{K_m} ML_m^{(n-m)+}$$

where K_m ($m \geq 1$) are the stepwise stoichiometric complex formation constants. Application of the general electromigration equation for the variation of the overall ion mobility $\bar{u}$ with the ligand concentration leads to (Eq.2):

$$\bar{u} = \frac{u^o_{M^{n+}} + \sum_{m=1}^{p} u^o_{ML_m^{(n-m)+}} \cdot [L^-]^m \cdot \prod_{j=1}^{m} K_j + \sum_{a=1}^{q} u^o_{M(OH)_a^{(n-a)+}} \cdot [H^+]^{-a} \cdot \prod_{j=1}^{a} K_j^{hyd}}{1 + \sum_{m=1}^{p} [L^-]^m \cdot \prod_{j=1}^{m} K_j + \sum_{a=1}^{q} [H^+]^{-a} \cdot \prod_{j=1}^{a} K_j^{hyd}}$$

where u_i^o are the absolute ion mobilities of the species acting in the equilibrium and K_a^{hyd} ($a \geq 1$) are the stepwise stoichiometric constants for the hydrolysis product.

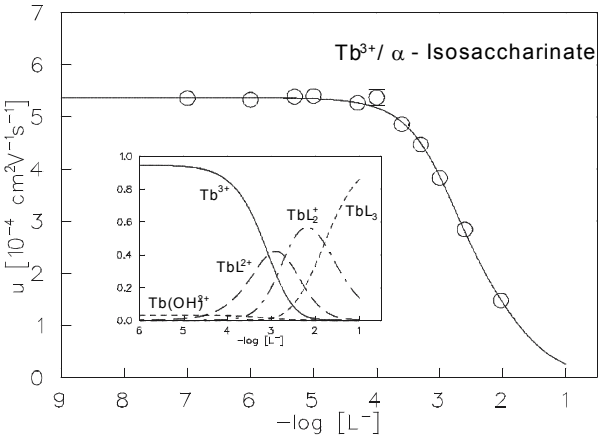

Figure 1. Overall ion mobility of $^{160}Tb^{3+}$ species versus α-isosaccharinate ligand concentration. NaL/NaOH/$NaClO_4$ electrolytes, T = 298.1, pH 7, μ = 0.1. The window in the plot shows the relative distribution of the species.

The values of K_n obtained from the fit of the experimental data with (Eq.2) are listed in Table 1. The K_n-values of the Tb^{3+}/α-ISA system were found to be similar to the Tb^{3+}/Gluconate system [4].

α-ISA cannot be purchased and must be prepared by a relatively long chemical route. Therefore, the use of gluconic acid, which is readily available in a relatively pure state, has been evaluated as an analogue of α-ISA.

Table 1. Stepwise complex formation constants for the complexation of terbium with α-ISA ligand.μ = 0.1, pH = 7, T = 298.1 K.

	$logK_1$	$logK_2$	$logK_3$	Ref.
Tb^{3+}/Gluconate	2.93(10)	2.58(10)	1.11(9)	[3]
Tb^{3+}/α-ISA	3.07(8)	2.69(11)	1.80(12)	This work

[1] 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). [2] Glaus, M. A., Van Loon , L. R., Achatz, S., Chodura, A., Fischer, K. Analytica Chemistry Acta **398** 111-122 (1999). [3] E. Mauerhofer et al., Institut für Kernchemie, Uni. Mainz, Jahresbericht 2001.