Hydrolysis of Co^{2+} in neutral aqueous perchlorate electrolytes investigated by means of electro-migration measurements

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Hydrolysis reactions are relevant processes and accompany most metal cations in aqueous systems. The reactions of the complexation with OH$^-$ ligand are commonly described by stoihiometric stability constants and are studied using a variety of analytical methods [1].

However, for most of the metal cations existing in ultra-low concentrations, what is the case for many no-carrier-added radioisotopes, the spectrum of applicable analytical methods is small.

It was shown elsewhere that precise stability constants of different systems can be obtained by means of electromigration techniques [2]. These data as well as resulting absolute overall ion mobilities of elements are of interest for the investigation of the phenomenon of migration and accumulation of various metals (radionuclides) in the natural environment.

Another aim of this work was to investigate the capacity of this technique to study processes in high alkaline solutions.

The no-carrier-added ^{57}Co ($T_{1/2}$ = 271.8 d) was purchased from AEA Technology QSA GmbH in 0.1 M HCl stock solution. The specific activity of the solution was 122 MBq/ml. An aliquot of 25 µl of the stock solution was mixed with 25 µl 0.1 M NaOH and then used for the electromigration measurement. The inert background perchlorate solutions with an overall ionic strength µ = 0.10 of the electrolyte media Na$^-$/OH$^-$/ClO$^-_4$ were prepared using p.a. chemicals (Merck) and analytical grade water. The pH of the electrolytes was measured by means of a pre-calibrated glass electrode using standard buffer solutions.

A bolus of 1.0 – 1.5 µl of the ^{57}Co solution (about 10^{-11} mol of Co^{2+}) was injected into the electromigration tube filled with the electrolyte. The experimental dependency of the overall ion mobility of Co^{2+} on the pH of the background electrolyte is shown in Fig. 1. The quantitative treatment of the experimental data of the absolute overall ion mobility, depending on the ligand concentration, is based on mechanism (1), which is generally accepted for the interpretation of the hydrolysis of M^{n+}:

$$M(OH)_{i-1}^{(n-i+1)+} + H_2O \xleftarrow{\quad K_i^{hyd} \quad} M(OH)_i^{(n-i)+} + H^+ \quad (1)$$
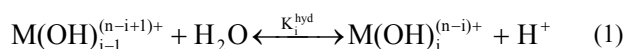
where K_i^{hyd} (i ≥1) are the stepwise stoichiometric hydrolysis constants. The overall ion mobility $\bar{u}$ represents the sum of the absolute individual ion mobilities u_i^0 of the species Co(OH)$_i^{(n-i)+}$ weighted with their relative concentration and may be expressed as a function of [H$^+$] concentration as follows:

$$\bar{u} = \frac{u_{Co^{2+}}^o + \sum_1^i u_{[Co(OH)_i]^{(2-i)+}}^o \cdot [H^+]^{-i} \cdot \prod_1^i K_i^{hyd}}{1 + \sum_1^i [H^+]^{-i} \cdot \prod_1^i K_i^{hyd}} \quad (2).$$

Figure 1. Overall ion mobility of ^{57}Co^{2+} species versus pH, Na$^+$/OH$^-$/ClO$^-_4$ electrolytes, T = 298.1 K, µ = 0.10. The window in the plot shows the relative distribution of the species.
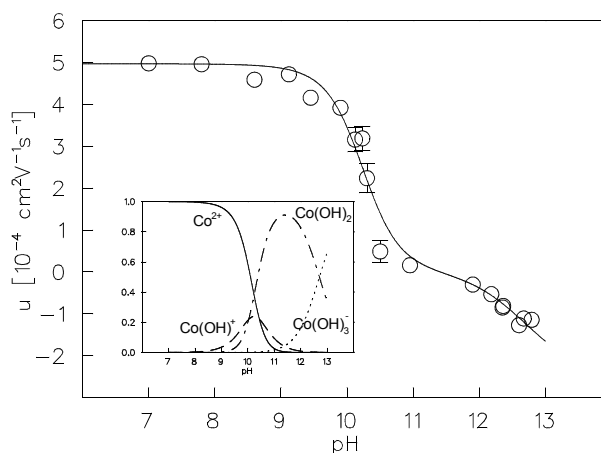
The absolute individual ion mobility of the species [Co(OH)$_i$]$^{(2-i)+}$ (i = 1,2,3) can be derived from the correlation observed between the ionic charge and the individual ion mobility of the species independent of the type of ligand [2], Table 1. The stepwise hydrolysis constants K_i^{hyd} obtained from the fit of the experimental data $\bar{u}$ = f([H$^+$]) with Eq (2) (solid line in Fig. 1) are summarised in Table 2 and compared with literature values [1].

The observed K_n-values are noticeable higher than literature values, however, the comparative analysis is complicated due to the scanty experimental data, especially for no-carrier-added systems. Finally, this work shows the possibility to use the method for investigation of ion mobilities in high alkaline solutions.

Table 1. The individual ion mobilities u_i^0 [10^{-4} cm^{2}V^{-1}s^{-1}] of [Co(OH)$_i$]$^{(2-i)+}$ - species. Background electrolyte: Na$^+$/OH$^-$/ClO$^-_4$, µ = 0.10, T = 298.1 K.

Species	u_i^0 [this work]	u_i^0 [3]
Co^{2+}	4.97	5.1
[Co(OH)]$^+$	2.49*	-
[Co(OH)$_2$]	0	-
[Co(OH)$_3$]$^-$	2.49*	-

* derived from the correlation between the ionic charge and the individual ion mobility [2] (see text)

Table 2. Stochiometric stability constants of Co^{2+} hydrolysis products. Background electrolyte Na$^+$/OH$^-$/ClO$^-_4$, µ = 0.1, T = 298.1 K.

logK$_1$	logK$_2$	logK$_3$	Ref.
-10.44(10)	-10.00(9)	-12.70(12)	This work
-9.65	-9.15	-12.70	[1]*
-9.90	-9.15	-12.45	[1]**

* at infinite dilution
** by evaluation µ = 0.1

[1] Baes, C. F., Mesmer, R. E. The Hydrolysis of Cations, Krieger Publisher Company, Inc., Florida (1986). [2] Rösch, F., Ditrich, S., Buklanov, G. V., Milanov, M., Khalkin, V. A. and Dreyer. R. Radiochem. Acta **48**, 205 – 211 (1989). [3] E. Mauerhofer, O. Kling and F. Rösch, Raiochim. Acta **89**, 537 (2001).