

Ion mobilities of Cs⁺ and Co²⁺ ions depending on the pH of inert aqueous electrolytes

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In order to study the influence of the water H-bonds on the transport properties of ions in solution, the absolute individual ion mobilities of the non-carrier-added [¹³⁷Cs]Cs⁺ and [⁵⁷Co]Co²⁺ ions at tracer-scale (10⁻¹⁰-10⁻¹² mol) were measured in Na(H)ClO₄ electrolytes ($\mu = 0.10$, $1 < \text{pH} < 7$, $T = 298.1 \text{ K}$) by mean of the on-line electromigration technique.

The experimental data were compared with the theoretical values given by the extended limiting law (ELL) [1] using as closest distance of approach between ions of opposite charge $a_{\text{NaClO}_4} = 4.04 \text{ \AA}$ and $a_{\text{HClO}_4} = 5.09 \text{ \AA}$ [2]. The variation of the experimental and calculated ion mobility with the pH is shown for the two ions in Fig.1. The experimental data were fitted using the following relation:

$$u = \frac{u_N + \beta_1^\Psi [\text{H}^+] u_A}{1 + \beta_1^\Psi [\text{H}^+]} f_{\text{el.}} \quad (1)$$

with u_N and u_A representing two levels of ion mobility in neutral and acidic solutions, $[\text{H}^+]$ the proton concentration, β_1^Ψ a stoichiometric constant of the system and $f_{\text{el.}}$ a function taking into account the change of the closest distance of approach between ions of opposite charge, when switching in perchlorate solution from Na⁺ (a_{NaClO_4}) to H⁺ (a_{HClO_4}). The function $f_{\text{el.}}$ was expressed as:

$$f_{\text{el.}} = \frac{1}{\mu} \left(\frac{a_{\text{HClO}_4}}{a_{\text{NaClO}_4}} [\text{H}^+] + (\mu - [\text{H}^+]) \right) \quad (2)$$

where $\mu = 0.10$ is the overall ionic strength of the electrolyte. The ratio $a_{\text{HClO}_4} / a_{\text{NaClO}_4}$ in (2) was used as free parameter. According to relation (1), the ion mobility in NaClO₄ is u_N and the one in HClO₄ is $u_A (a_{\text{HClO}_4} / a_{\text{NaClO}_4})$.

The results obtained from the fit of the experimental data are listed together with theoretical values in Tab. 1.

As shown in Fig.1 the variation of the experimental ion mobility may be shared in 3 zones whose characteristics depend on the nature of the hydrated ion. In zone 1, ($3.5 < \text{pH} < 7$ for Cs⁺, $5 < \text{pH} < 7$ for Co²⁺), the ion mobility is constant and its value is in agreement with the theoretical value given by the ELL. In zone 2 ($2 < \text{pH} < 3.5$ for Cs⁺, $2 < \text{pH} < 5$ for Co²⁺), the ion mobility decreases for increasing $[\text{H}^+]$ concentration. In zone 3 ($\text{pH} < 2$ for Cs⁺ and Co²⁺), a small increase of the ion mobility is observed which is in qualitative agreement with the ELL. The decrease of the ion mobilities in zone 2 and 3 may be explained by an increase of the frictional forces exerted on the ions due to a change of the nature of the hydrogen bonds in the water. As the proton concentration increases, the following water cluster ions are formed $\text{H}_3\text{O}^+ \rightarrow \text{H}_5\text{O}_2^+ \rightarrow (\text{H}_7\text{O}_3^+) \rightarrow \text{H}_9\text{O}_4^+$ [3-6] modifying the structure of water and thus the ion-water interaction. The different behaviour of Cs⁺ and Co²⁺ ions with regards to the pH of the electrolyte lies in the different structure and properties of their hydration shells.

< pH < 5 for Co²⁺), the ion mobility decreases for increasing $[\text{H}^+]$ concentration. In zone 3 (pH < 2 for Cs⁺ and Co²⁺), a small increase of the ion mobility is observed which is in qualitative agreement with the ELL. The decrease of the ion mobilities in zone 2 and 3 may be explained by an increase of the frictional forces exerted on the ions due to a change of the nature of the hydrogen bonds in the water. As the proton concentration increases, the following water cluster ions are formed $\text{H}_3\text{O}^+ \rightarrow \text{H}_5\text{O}_2^+ \rightarrow (\text{H}_7\text{O}_3^+) \rightarrow \text{H}_9\text{O}_4^+$ [3-6] modifying the structure of water and thus the ion-water interaction. The different behaviour of Cs⁺ and Co²⁺ ions with regards to the pH of the electrolyte lies in the different structure and properties of their hydration shells.

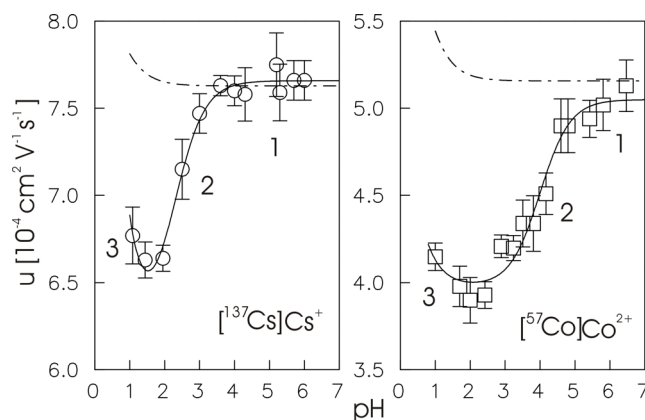


Figure 1: Individual ion mobilities of the non-carrier-added Cs⁺ and Co²⁺ ions versus pH of the inert electrolyte. Electrolytes: Na(H)ClO₄, $\mu = 0.10$, $T = 298 \text{ K}$. The solid line correspond to the fit of the data with eq. (1). The dashed line represents the ELL.

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Table 1.

Results of fit according to eq.(1) of the experimental data for Cs⁺ and Co²⁺ ions given in Fig. 1 and theoretical values.

Electrolytes: Na(H)ClO₄, $\mu = 0.10$, $T = 298 \text{ K}$. u in $10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$, β_n^Ψ in $\text{l}^{-1} \text{ mol}$.

ion	Experimental						Theory		
	u_N	u_A	$\lg \beta_1^\Psi$	u_{NaClO_4}	u_{HClO_4}	$\frac{a_{\text{HClO}_4}}{a_{\text{NaClO}_4}}$	u_{NaClO_4}	u_{HClO_4}	$\frac{a_{\text{HClO}_4}}{a_{\text{NaClO}_4}}$
Cs ⁺	7.66(2)	6.11(19)	2.25(28)	7.66(2)	6.78(32)	1.11(4)	7.63	7.81	1.25
Co ²⁺	5.05(5)	3.98(5)	4.00(29)	5.05(5)	4.14(13)	1.04(4)	5.16	5.44	1.25

