Levels of Ion Mobilities of Divalent Ions According to the pH of Inert Aqueous Electrolytes

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The existence of two different levels of ion mobilities in neutral (pH > 5) and acidic (pH < 3) $Na(H)ClO_4$ electrolyte solutions ($\mu = 0.10$, T = 298 K) was found for the trivalent lanthanides and actinides ions, except for Eu^{3+} and Cf^{3+}, by Rösch et al. [1]. A first interpretation for the change of the ion mobility with the H^+ concentration was done using the following phenomenological equation:

$$u_{\text{Neutral}} + n\,H^+ \overset{\beta_n^\psi}{\Leftrightarrow} u_{\text{Acidic}} \qquad (1)$$

where u_{Neutral} and u_{Acidic} correspond to the two levels of ion mobility in neutral and acidic solution. β_n^ψ is the stoichiometric stability constant of the system.

Within the context of a systematic study of this phenomenom the ion mobility of carrier-free $^{57}Co^{2+}$ ions was measured in dependence of the pH of $Na(H)ClO_4$ electrolytes at $\mu = 0.10$, T = 298 K by means of the on-line electromigration technique [2]. Experimental migration data were corrected for the electroosmosis using expression (1) in [3]. In addition the absolute migration data of $^{87m}Sr^{2+}$ obtained for the same electrolyte in a previous experiment [4] were analysed for comparison. The variation of the absolute ion mobility with the pH is shown for the two divalent ions in Fig.1. In acidic solution with pH lower than 3 the of ion mobilities are constant. Then the ion mobility increases with increasing pH (3 > pH > 5) and a new constant level is reached at pH higher than 5 up to the beginning of hydrolysis reactions. The lowering of the ion mobility in acidic solution is due to an increase of the micro-viscosity of water molecules at the vicinity of the ion i.e. increase of the hydration sphere. The results obtained from the fit of the data with eq. (1), varying the number n of hydrogen cations, are listed in Tab.1.

Table 1. Results of the fit according to eq.(1) of the migration data for Co^{2+} and Sr^{2+} ions given in Fig.1. Electrolytes: $Na(H)ClO_4$, $\mu = 0.10$, T = 298 K.
u_{Neutral} and u_{Acidic} in 10^{-4} $cm^2\,s^{-1}\,V^{-1}$, β_n^ψ in $l^n\,mol^n$

Ion	n	u_{Neutral}	u_{Acidic}	$\lg\beta_n^\psi$	$\frac{1}{n}\lg\beta_n^\psi$
Co^{2+}	1	5.36(6)	4.32(4)	4.07(12)	4.07(12)
	2	5.30(6)	4.39(5)	8.26(13)	4.13(13)
	3	5.29(6)	4.42(5)	12.51(20)	4.17(20)
Sr^{2+}	1	5.96(7)	5.08(10)	3.13(14)	3.13(14)
	2	5.93(5)	5.11(7)	6.15(20)	3.08(20)
	3	5.93(5)	5.13(6)	9.21(27)	3.07(27)

The values of $\lg\beta_n^\psi$ reflect the change of the frictional forces between the ions and the water molecules. As shown in Fig.2, the ratio $\lg\beta_1^\psi/N$, where N is the number of water molecules in the first hydration shell, is correlated with the charge density of the ion.

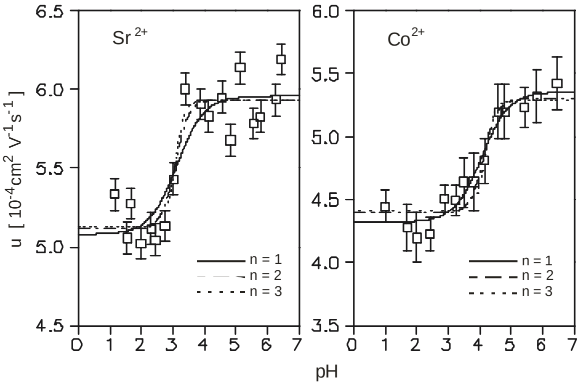

Fig. 1. Individual ion mobilities of the carrier-free $Sr^{2+}$and Co^{2+} ions versus pH of the inert electrolyte. Electrolytes: $Na(H)ClO_4$, $\mu = 0.10$, T = 298 K. The curves correspond to the fit of the data with equ. (1) for n = 1, 2, 3.

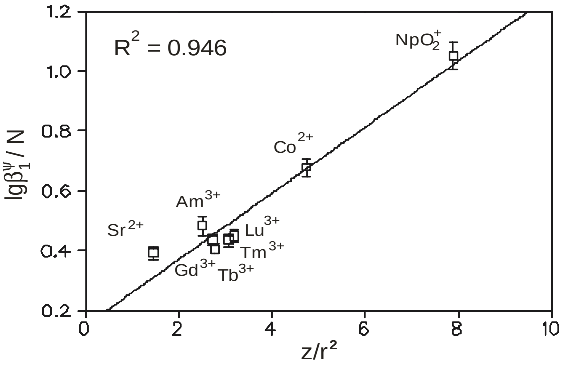

Fig. 2. The correlation between $\lg\beta_1^\psi/N$ and Z/r^2; for the radius r, the CN = 8 values are used for Lan^{3+} and Am^{3+}; that of CN = 6 for Co^{2+} and Sr^{2+} and that of CN = 4 for NpO_2^+. Z of Np(V) was taken as 2.3 [5]. $\lg\beta_1^\psi$ for NpO_2^+ was taken in [6].

References

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