

## Ion Mobility of Lu<sup>3+</sup> in Aqueous Perchlorate Electrolytes of high overall ionic strength.

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The properties of the ions in aqua-solutions such as diffusion mobility and conductivity are important parameters in solution chemistry and have been extensively studied from the beginning of 20<sup>th</sup> century. However, only limited experimental data are available about absolute ion mobilities especially for strong concentrated solutions. Furthermore, for Lu<sup>3+</sup>-cation the data about the limiting (at infinite dilution) ion mobility  $u_i^0$  are absent [1].

The dependence of the absolute individual ion mobility of Lu<sup>3+</sup>-cation on the ionic strength of perchlorate aqua-solution was investigated by means of electromigration measurements of non-carrier-added <sup>172</sup>Lu<sup>3+</sup>.

<sup>172</sup>Lu ( $T_{1/2} = 6.7$  d) was separated from a <sup>172</sup>Hf-<sup>172</sup>Lu generator in 6 M HCl solution [2]. The hydrochloric acid was removed by evaporation and the residue was then dissolved in 0.01 M HClO<sub>4</sub>.

The perchlorate aqua-solutions with different ionic strength were prepared using p.a. NaClO<sub>4</sub> (Merck) and analytical grade water.

The volume of the <sup>172</sup>Lu<sup>3+</sup> solution injected into the electrolyte in the electromigration tube was about 1-2 μL with total activity about 300 KBq corresponding to a metal amount in the migration zone of  $\approx 10^{-12}$  mol. Measurements of absolute individual ion mobilities were performed with an electric field intensity of 2-10 V/cm at temperature of 298.1K.

The experimental results obtained for Lu<sup>3+</sup> are illustrated in Figure 1. The ion mobility of Lu<sup>3+</sup> decreases with increasing of ionic strength until  $\mu \approx 0.5$  and again increases.

The limiting ion mobility  $u_i^0$  ( $m^2V^{-1}s^{-1}$ ) can be calculated using the Stokes-Einstein law in its microscopic form [3]:

$$u_i^0 = \frac{e|z_i|}{6\pi\tilde{\eta}_i^0 r_i} \quad (1)$$

where  $e$  is the elementary charge ( $1.6022 \times 10^{-19}$  C),  $z_i$  the charge number of the ion,  $r_i$  the ionic radius (m) and  $\tilde{\eta}_i^0$  the viscosity of the water molecules in the first hydration shell of the ion (ion micro-viscosity). The ion micro-viscosity represents a complicated exponential function of the surface charge density of the ion  $\sigma_i = |z_i|e/4\pi r_i^2$  ( $C \cdot m^{-2}$ ):

$$\frac{1}{\tilde{\eta}_i} = \frac{1}{\tilde{\eta}_i^0} \ln[1 - [e^{-4\pi\sigma} (e^{-\sigma_s} (e^{p\sigma} - e^{q\sigma}) + e^{q\sigma} - 1)]] \quad (2)$$

where  $p = 11.65$  ( $m^2 C^{-1}$ ),  $q = 12.52$  ( $m^2 C^{-1}$ ) and  $\sigma_s = 0.24$  ( $C \cdot m^{-2}$ ).

The corresponding calculated values of  $\tilde{\eta}_i^0$  and  $u_i^0$  for Lu<sup>3+</sup> is given in Table 1.

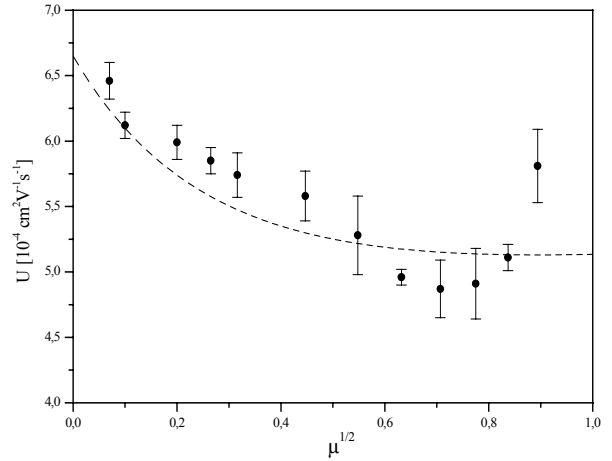


Figure 1. Dependence of individual ion mobility of n.c.a. Lu172 on  $\mu^{1/2}$  of NaClO<sub>4</sub> electrolyte at 298.1 K; extended limiting law Eq. (2) (dotted line).

According to Onsager theory (1945) and to correction proposed by Stokes the absolute individual ion mobility may be given by the extended limiting law as a function of the overall ionic strength of electrolyte:

$$u_i = u_i^0 - \frac{2.802 \times 10^6 z^2 u_i^0 (1 - \sqrt{d(w)})}{(\epsilon T)^{3/2}} \times \frac{\sqrt{\mu}}{(1 + ka)(1 + ka/\sqrt{2})} \quad (3)$$

where  $\epsilon$  is the dielectric constant of the solvent,  $d(w)$  a mobility function,  $k = \sqrt{\mu} / 3.041 \cdot 10^{-8}$  and  $a$  the closest distance of approach between ions of opposite charge ( $a = 4.04$  Å for NaClO<sub>4</sub>).

In order to check the applicability of the Onsager theory to this system, the individual ion mobility values of Lu<sup>3+</sup> are calculated on the basis of this theory and compared with the experimental data (dotted line in Fig. 1).

The  $u_{Lu^{3+}}^0$ -value calculated by Eq. (1-2) is in good agreement with experimental points. We have also obtained the increasing of individual ion mobility which is not predicted by the Onsager theory in the range of overall ionic strength of the electrolyte over 0.5.

Table 1. Limiting ion mobility  $u^0$  ( $10^{-8} m^2V^{-1}s^{-1}$ ) of Lu<sup>3+</sup>;  $r$  ionic radius [1].

Ion	$r$ [ $10^{-10}$ m]	$\tilde{\eta}_i^0$ ( $kg^{-1}m^{-1}$ ) (eqn2)	$u^0$ (cal.)
Lu <sup>3+</sup>	0.86	44.69	6.64

[1] Handbook of Chemistry and Physics, 78<sup>th</sup> Ed., CRC Press (1978-1998). [2] N. Lebedev et. al, this report. [3] K. Zhernosekov, F. Rösch, this report.