

Ion Mobility of Lu³⁺ in Aqueous Perchlorate Electrolytes of high overall ionic strength.

K. Zhernosekov, E. Mauerhofer, F. Rösch

Institut für Kernchemie, Johannes Gutenberg-Universität Mainz

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 20th century. However, only limited experimental data are available about absolute ion mobilities especially for strong concentrated solutions. Furthermore, for Lu³⁺-cation the data about the limiting (at infinite dilution) ion mobility u⁰ are absent [1].

The dependence of the absolute individual ion mobility of Lu³⁺-cation on the ionic strength of perchlorate aqua-solution was investigated by means of electromigration measurements of non-carrier-added ¹⁷²Lu³⁺.

¹⁷²Lu ($T_{1/2} = 6.7$ d) was separated from a ¹⁷²Hf-¹⁷²Lu generator in 6 M HCl solution [2]. The hydrochloric acid was removed by evaporation and the residue was then dissolved in 0.01 M HClO₄.

The perchlorate aqua-solutions with different ionic strength were prepared using p.a. NaClO₄ (Merck) and analytical grade water.

The volume of the ¹⁷²Lu³⁺ 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 298.1 K.

The experimental results obtained for Lu³⁺ are illustrated in Figure 1. The ion mobility of Lu³⁺ decreases with increasing of ionic strength until $\mu \approx 0.5$ and again increases.

The limiting ion mobility u_i^0 ($\text{m}^2\text{V}^{-1}\text{s}^{-1}$) 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 (1.6022×10^{-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 $\sigma_i = |z_i|e/4\pi r_i^2$ ($\text{C} \cdot \text{m}^{-2}$):

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

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

The corresponding calculated values of $\tilde{\eta}_i^0$ and u_i^0 for Lu³⁺ is given in Table 1.

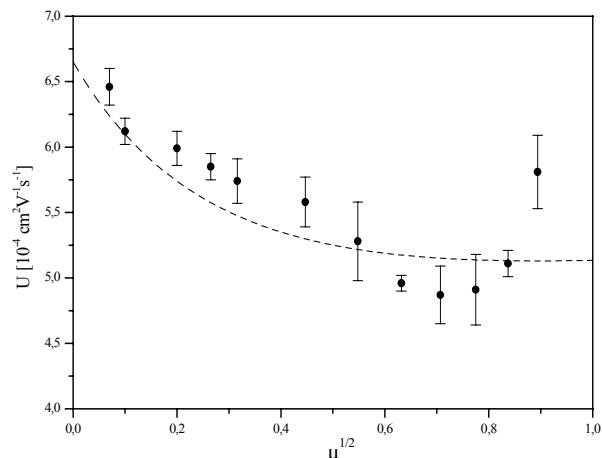


Figure 1. Dependence of individual ion mobility of n.c.a. Lu172 on $\mu^{1/2}$ of NaClO₄ electrolyte at 298.1 K; extended limiting law Eq. (2) (dotted line).

According to Onsager theory (1945) and to correction proposed by Stokes the absolute individual ion mobility may be given by the extended limiting low 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 ϵ 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 ($a = 4.04 \text{ \AA}$ for NaClO₄).

In order to check the applicability of the Onsager theory to this system, the individual ion mobility values of Lu³⁺ are calculated on the basis of this theory and compered with the experimental data (dotted line in Fig. 1).

The $u_{\text{Lu}^{3+}}^0$ -value calculated by Eq. (1-2) is in good agreement with experimental poins. 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 ($10^{-8} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$) of Lu³⁺; r ionic radius [1].

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

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