Limiting ionic conductivity of actinyl ions

E. Mauerhofer, F. Rösch
Institut für Kernchemie, Johannes Gutenberg-Universität Mainz

The assessment of the limiting ionic conductivity in pure water λ^0 of pentavalent and hexavalent actinide ions is important for the understanding of their ionic transport in water (ion-water interactions) as well as for the determination of their total hydration numbers (number of water molecules in the ion's primary and secondary hydration shells). The values of λ^0 for the actinyl ions UO_2^{2+}, NpO_2^{+} and PuO_2^{2+} have been determined employing different experimental methods and taking into account necessary corrections for hydrolysis and for other ionic species present in the system studied (Table 1, column 6) [1,2]. For the other actinyl ions, UO_2^{+}, NpO_2^{2+}, PuO_2^{+}, AmO_2^{+} and AmO_2^{2+} no experimental data on λ^0 are available in particularly due to the instability of these ions in aqueous solutions (disproportionation, reduction by action of own α-radiation) which makes the study of their individual transport properties difficult. In this context a pertinent model to calculate the limiting ionic conductivity of the actinyl ions appears of prime importance.

According to Stoke's law [3,4], the limiting ionic conductivity of non spherical shaped actinyl ions MO_2^{n+} (n = 1, 2) having a random orientation to their direction of migration can be expressed by:

$$\lambda^0 = \frac{0.820\, z_M}{\theta\, \eta_i^s\, r_i^s} \qquad (1)$$

with z_M the effective cationic charge of the metal ion M [5], θ a strucural factor for deviations from the spherical geometry with regards to the frictional forces, η_i^s the equivalent spherical microviscosity and r_i^s the equivalent spherical radius for the actinyl ion. The use of the effective cationic charge z_M in Eq.(1) and not the formal charge n of the actynil ion could be supported by the following reasons : 1) The water molecules in the first hydration shell are coordinated to the metal ion M. 2) Due to its strong electrostatic field, although shielded by the oxygen atoms, M is able to build a second hydration shell. 3) The total number of water molecules in the hydration shell is connected to the size of the aquo-ion (Stokes' radius or hydrated radius) and thus to the transport properties of the ion.

The value of r_i^s (Tab.1) was simply calculated from the volume of the bare ion obtained in [6]. Using the general relation given in [4], the structural factor θ (Tab.1) for actinyl ions described by ellipsoids of revolution (O-M-O as axis of revolution) having a random orientation to their direction of migration may be expressed by:

$$\theta = \frac{\sqrt{1-(r_M/d_{M-O}+\delta)^2}}{(r_M/d_{M-O}+\delta)^{2/3}\, \mathrm{Ln}\left(\frac{(d_{M-O}+\delta)(1+\sqrt{1-(r_M/d_{M-O}+\delta)^2}}{r_M}\right)} \qquad (2)$$

where r_M, d_{M-O} and δ are defined in [6]. The value of η_i^s (Tab.1) was estimated by inserting z_M and r_i^s in the following analytical expression:

$$\eta_i = [2.42(\ln(z/r^2))^2 + 15.49\ln(z/r^2) + 17.84]10^{-4} \qquad (3)$$

which was deduced from the fit of the plot η_i versus z/r^2 for the spherical cations. The values of η_i for the latter were determined using Eq.(1) and the corresponding λ^0-values (T = 298.15 K) from [7]; for the lanthanide ions from [8,9], with θ = 1, r_i^s = , ionic radius (CN = 6, except for the lanthanides ions and Ra^{2+} CN = 8) [10], z_M = formal charge of the ion As shown in Tab.1 the λ^0-values obtained for UO_2^{2+}, NpO_2^{+} and PuO_2^{2+} are in good agreement with the experimental values. This indicates on the validity of the model employed in which the actinyl ions are defined by the set of parameters [r_i^s, z_M, θ].

[1] G. Marx and W. D. Wittke, *Z. Naturforsch.* 32a, (1977) 186. [2] F. Arndt and G. Marx, *Z. Naturforsch*. 36a, (1981) 1019. [3].G. G. Stokes, *Trans. Cambridge Philo. Soc.*, 8 (1845) 287. [4] R. H. Stokes and R. Mills, *Viscosity of electrolytes and related properties*, Pergamon Press (1965) [5] H. Moriyama et al., *Radiochim. Acta* 87, (1999) 97. [6] E. Mauerhofer and F. Rösch, *Primary hydration numbers of actinyl ions,* previous report. [7] *Handbook of the chemistry and physics*, 78th Ed. CRC Press (1997/1998). [8] B. Fourest et al, *Radiochim. Acta* 46, (1989) 131. [9] B. Fourest et al, *Radiochim. Acta* 36, (1984) 191. [10] R. D. Shannon *Acta Crystallogr.* A32 (1976) 751.

Table 1.
Data used for the determination of the limiting ionic conductivity λ^0 of the actinyl ions at 298.15 K.
See text for the definition of r_i^s, θ and η_i^s. a) [1], b) [2]

Ion	r_i^s [Å]	θ	η_i^s $10^{-4}kg^{-1}s^{-1}$	λ^0 $cm^2\Omega^{-1}val^{-1}$	$\lambda^0_{exp.}$
UO_2^{+}	1.105(4)	1.12(2)	28.2(1.0)	52.6(1.9)	-
UO_2^{2+}	1.070(4)	1.12(2)	36.5(1.3)	60.6(2.1)	57(2)$^{a)}$
NpO_2^{+}	1.100(4)	1.13(2)	29.6(1.0)	54.0(1.8)	51(1)$^{b)}$
NpO_2^{2+}	1.065(4)	1.13(2)	36.3(1.5)	59.9(2.5)	-
PuO_2^{+}	1.095(4)	1.13(2)	30.7(1.1)	55.0(2.0)	-
PuO_2^{2+}	1.059(4)	1.13(2)	36.6(1.5)	59.5(2.4)	59(2)$^{b)}$
AmO_2^{+}	1.097(4)	1.13(2)	27.3(1.0)	50.7(1.9)	-
AmO_2^{2+}	1.051(4)	1.14(2)	34.2(1.5)	55.6(2.4)	-