Secondary and total hydration numbers of actinyl ions

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The secondary hydration numbers were calculated as follows:

$$H = \frac{V_{hyd,2} - V_{hyd,1}}{V_{H_2O,2}} \qquad (1)$$

where $V_{hyd,2}$ is the total volume of the aquo ion including primary and secondary hydration sphere, $V_{hyd,1}$ the volume of the aquo ion's primary hydration sphere and $V_{H_2O,2}$ the volume of a water molecule in the second hydration shell. The total volume of the aquo ion may be given by:

$$V_{hyd,2} = \frac{4}{3}\pi r_h^3 \qquad (2)$$

where r_h is the total hydrated radius of the ion. Using the calibration procedure proposed by Nightingale [1], r_h may be calculated from the Stockes' radius r_s with the following analytical expression:

$$r_h = 2.672 + 0.581 r_s - 0.0665 r_s^2 + 0.00961 r_s^3 \qquad (3)$$

The Stokes' radius r_s for the actinyl ions was calculated from the Stokes' law as follows:

$$r_s = \frac{0.820\, z_M}{\theta \eta^0 \lambda^0} \qquad (4)$$

with z_M the effective cationic charge of the metal ion M [2], θ the structural factor defined for the actinyl ions in [3], λ^0 the limiting ionic conductivity of the actinyl ions [3] and $\eta^0 = 8.903\ 10^{-4}$ $kg^{-1}s^{-1}$ the viscosity of pure water at 298.15 K. The values of r_s, r_h and $V_{hyd,2}$ are listed in Table 1 together with the values of $V_{hyd,1}$ calculated in [4]. The volume occupied by a water molecule in the second hydration shell, $V_{H_2O,2}$, was set to 30 Å^3 since as demonstrated in [5] electrostriction effects outside the primary hydration shell are negligible. The values of H obtained as well as the total hydration numbers, h = N+H, for the actinyl ions are given in Tab. 1. For comparison the values of N, H and h for the spherical actinide ion (Tab.1) were calculated by the same way as for the actinyl ions using ionic radii CN = 8, and effective charges from [2]. As shown in Fig.1, the entropy of hydration which reflects the effect of ions on the structure of water, is well correlated with the total number of water molecule in the hydration sphere.

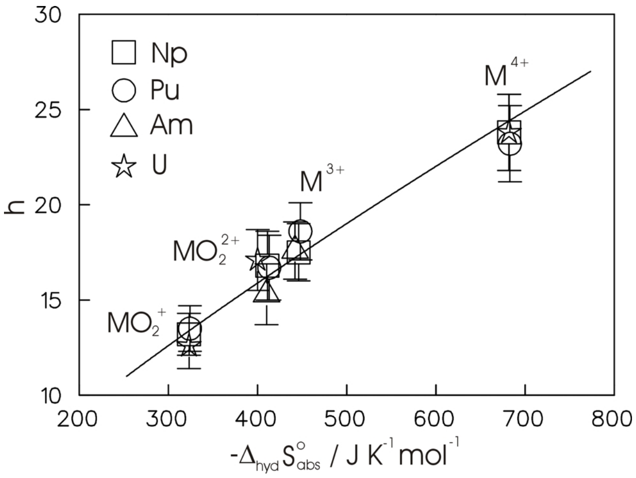

Figure 1: total hydration number, h, plotted against the standard molar entropy of hydration, $\Delta_{hyd}S^{o}_{abs}$ [6], for actinides ions.

[1] E. R. Nightingale, J. Phys. Chem. 63, (1959) 1381. [2] H. Moriyama et al., *Radiochim. Acta* 87, (1999) 97. [3] E. Mauerhofer and F. Rösch*, Limiting ionic conductivity of actinyl ions*, previous report. [4] E. Mauerhofer and F. Rösch*, Primary hydration numbers of actinyl ions*, previous report. [5] R. L. Hahn, J. *Phys. Chem*. 92, (1988) 1668. [6] *Handbook on the physics and chemistry.of the actinides*, Vol 18. North-Holland (1994).

Table 1. Data used for the determination of the hydration numbers H of actindes ions MO_2^{n+} and M^{n+}.
λ^0 limiting ionic conductivity, r_s Stockes' radius, r_h total hydrated radius, $V_{hyd,1}$ volume of the aquo ion's primary hydration sphere, $V_{hyd,2}$ total volume of the aquo ion. N primary hydration number, h = N + H total hydration number

Ion	λ^0 $cm^2\Omega^{-1}val^{-1}$	r_s [Å]	r_h [Å]	$V_{hyd,1}$ [Å^3]	$V_{hyd,2}$ [Å^3]	N	H	h
UO_2^{+}	52.6(1.9)	3.50(13)	4.30(16)	93(4)	333(37)	4.6(2)	8.0(1.0)	12.6(1.2)
UO_2^{2+}	60.6(2.1)	4.39(16)	4.75(17)	90(4)	449(48)	5.1(2)	12.0(1.4)	17.1(1.6)
NpO_2^{+}	54.0(1.8)	3.66(12)	4.38(14)	94(4)	352(34)	4.6(2)	8.6(9)	13.2(1.1)
NpO_2^{2+}	59.9(2.5)	4.34(18)	4.73(20)	91(4)	443(56)	5.1(2)	11.7(1.6)	16.8(1.8)
PuO_2^{+}	55.0(2.0)	3.77(13)	4.43(15)	95(4)	364(37)	4.5(2)	9.0(1.0)	13.5(1.2)
PuO_2^{2+}	59.5(2.4)	4.35(18)	4.73(19)	91(4)	443(53)	5.0(2)	11.7(1.5)	16.7(1.7)
AmO_2^{+}	50.7(1.9)	3.36(12)	4.24(15)	95(4)	319(34)	4.5(2)	7.5(9)	12.0(1.1)
AmO_2^{2+}	55.6(2.4)	4.04(18)	4.57(20)	91(4)	400(52)	5.0(2)	10.3(1.4)	15.3(1.6)
U^{4+}	78.0(2.8)	5.16(18)	5.22(18)	156(5)	595(61)	9.1(4)	14.7(1.6)	23.8(2.0)
Np^{3+}	67.5(2.2)	4.27(14)	4.69(15)	173(5)	432(41)	8.9(4)	8.6(9)	17.5(1.3)
Np^{4+}	77.5(2.5)	5.16(17)	5.22(17)	153(5)	595(58)	9.0(4)	14.7(1.5)	23.7(1.9)
Pu^{3+}	69.4(2.3)	4.46(15)	4.79(16)	172(5)	460(46)	9.0(4)	9.6(1.0)	18.6(1.4)
Pu^{4+}	77.1(2.5)	5.10(16)	5.18(16)	152(5)	582(54)	8.9(4)	14.3(1.5)	23.2(1.9)
Am^{3+}	67.0(2.2)	4.30(14)	4.70(15)	168(5)	435(42)	8.7(4)	8.9(9)	17.6(1.3)