Primary hydration numbers of actinyl ions

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Knowledge of the structural characteristics of actinyl ion aqua complexes , i.e, the number of water molecules N in the inner hydration shell are essential for the interpretation of the physical-properties of actinides ions.
The primary hydration numbers were calculated as follows:

$$N = \frac{V_{hyd,l} - V_{ion}}{V_{H_2O,l}} \qquad (1)$$

where V_{ion} is the volume of the bare ion, $V_{hyd,l}$ the volume of the aquo ion's primary hydration sphere and $V_{H_2O,l}$ the volume of a water molecule in the first hydration shell. As simple geometric model, the MO_2^{n+} (n = 1, 2) ions were described by ellipsoids of revolution with the axis O-M-O as axis of revolution and the volume of the bare ion expressed by:

$$V_{ion} = \frac{4}{3}\pi r_M^2 (d_{M-O} + \delta) \qquad (2)$$

with r_M the ionic radius of the central metal atom M (CN = 6) [1], d_{M-O} the interatomic distance in the actinyl ion [2] and δ an additional length to the interatomic distance taking into account the space occupied by the oxygen atoms. The value of δ was estimated from the lattice parameter a_0 of the corresponding actinide dioxide MO_2 (CaF_2-type) [3] and using the value $r_{O^{2-}}$ = 1.38 Å (CN = 4) as follows:

$$\delta = \frac{2 r_{O^{2-}}}{\sqrt{3}\, a_0} d_{M-O} \qquad (3)$$

Because of the partial shielding of the central metal atom M by the oxygen atoms, the first hydration shell was supposed to extend from M with the thickness Δr_1 only in the plane perpendicular to the O-M-O axis (equatorial plane). Thus using Eq.(2) the volume of the aquo ion's first hydration sphere may be written

$$V_{hyd,l} = V_{ion} \left(1 + \frac{\Delta r_1}{r_M}\right)^2 \qquad (4)$$

According to [4], the value of Δr_1 was set to 2.33(7) Å independently of the charge and size of the ion. The volume occupied by a water molecule in the hydration shell was calculated using the Conway's formula [5] which takes into account electrostriction (reduction of the volume) caused by the charge of the ion:

$$V_{H_2O,l} = \left[K\left(\frac{z_M e}{\varepsilon_0 \varepsilon_r \chi^2}\right)^2 + 1\right]^{-G} V_{H_2O} \qquad (5)$$

with z_M the effective cationic charge of M [6], ε_r the dielectric constant of water, $\chi = (r_M + \Delta r_1/2)$ the mean distance from the ion, K = 1.1 10^{-11}, G = 0.15 and V_{H_2O} = 30 Å^3 the liquid volume of a bulk water molecule.
The data used for calculations are listed together with the resulting values of N in Table 1. The calculations reveal 5 water molecules coordinated to the central actinde ion M in MO_2^{n+} which is in good agreement with recent published data based on experimental measurements [7,8].

[1] G. R. Choppin, *Radiochim. Acta* 32, (1983) 143. [2] Y. Marcus and A. Loewenschuss, *J. Chem., Faraday Trans. 1* 82, (1986) 2873. [3] *Handbook on the phys. and chem.of the actinides*, Vol 18. North-Holland (1994). [4] R. L. Hahn, J. *Phys. Chem*. 92, (1988) 1668. [5] B. E. Conway, *Ionic Hydration in Chemistry and Biophysics,* Elsevier, Amsterdam (1981). [6] H. Moriyama et al., *Radiochim. Acta* 87, (1999) 97. [7] A. Yu. Garnov et al., *Radiochemistry*, 38, No. 5 (1996) 402. [8] N. Bardin et al, *Radiochim. Acta* 83, (1998) 189.

Table 1. Data used for the determination of the hydration numbers N of the actinyl ions MO_2^{n+}.
r_M, z_M ionic radius (CN = 6) and effective charge of the metal ion M, d_{M-O} interatomic distance in the actinyl ion, a_0 lattice parameter of the actinide dioxide MO_2 , δ additional length to d_{M-O} for the space occupied by the oxygen atoms, V_{ion} volume of the bare ion, $V_{hyd,l}$ volume of the aquo ion's primary hydration sphere, $V_{H_2O,l}$ volume of a water molecule in the first hydration sphere.

Ion	r_M [Å]	z_M	d_{M-O} [Å]	a_0 [Å]	δ [Å]	V_{ion} [Å^3]	$V_{hyd,l}$ [Å^3]	$V_{H_2O,l}$ [Å^3]	N
UO_2^{+}	0.76	2.24	1.81(2)	}5.470	0.527(6)	5.65(6)	93(4)	18.8(4)	4.6(2)
UO_2^{2+}	0.73	3.23	1.78(2)		0.518(6)	5.13(6)	90(4)	16.8(3)	5.1(2)
NpO_2^{+}	0.75	2.40	1.83(2)	}5.425	0.537(6)	5.58(6)	94(4)	18.4(4)	4.8(2)
NpO_2^{2+}	0.72	3.19	1.80(2)		0.529(6)	5.06(6)	91(4)	16.8(3)	5.1(2)
PuO_2^{+}	0.74	2.55	1.85(2)	}5.396	0.546(6)	5.50(6)	95(4)	18.0(4)	5.0(2)
PuO_2^{2+}	0.71	3.18	1.82(2)		0.537(5)	4.98(5)	91(4)	16.7(3)	5.2(2)
AmO_2^{+}	0.73	2.08	1.86(2)	}5.374	0.551(6)	5.38(6)	95(4)	19.0(4)	4.7(2)
AmO_2^{2+}	0.70	2.78	1.83(2)		0.543(5)	4.87(5)	91(4)	17.4(3)	5.0(2)