ADDITIONS AND CORRECTIONS

2005, Volume 109A

Grigory A. Shamov and Georg Schreckenbach*: Density Functional Studies of Actinyl Aquo Complexes Studied Using Small-Core Effective Core Potentials and a Scalar Four-Component Relativistic Method

Page 10961. In our article, among other topics we have calculated the free energies of hydration of actinyl(V) and (VI) cations according to the reaction:

$$AnO_2^{n+} + 5H_2O(aq) \rightarrow [AnO_2(H_2O)_5]^{n+}(aq) \qquad (n = 1, 2) \qquad (4)$$

(The equation number corresponds to the one in the original paper.)

For comparison of the calculated solvation free energies of actinyls with the experimental ones, the latter were estimated from experimental hydration enthalpies by Gibson et al.[1] and hydration entropies. For actinyl dications, the value of the uranyl(VI) hydration entropy was estimated by Marcus et al.,[2,3] which is −78.6 cal/(mol·K). For actinyl monocations, the value of 0.0 cal/(mol·K) was taken on the grounds that it is known[3] that monocations usually have higher (i.e., less negative) values for the hydration entropy than dications of comparable nature.

Unfortunately, in the Table 8 of our original article, the negative sign of the entropy was lost, and thus the values of the "experimental" ΔG_{298}^{hydr} of hydration were incorrectly calculated to be about −415 kcal/mol. We provide the fixed Table 8 in the present correction. Also the corresponding passage in the text of the original article should read as "All of the above gives us 'experimental' values for ΔG_{298}^{hydr} equal to −374.5 and −169.5 kcal/mol for the uranyl(VI) and -(V), respectively."

Considering that, some conclusions of the original paper have to be modified. First, for the mixed explicit-continuum solvation calculations (Table 7 of the original text), the closest value to the "experimental" ΔG_{298}^{hydr} will now be for the case of the complex including the first coordination sphere (five waters) of actinyls only. Adding extra second-coordination sphere waters does somewhat overestimate the calculated ΔG_{298}^{hydr} , although the influence is modest. Second, for the free energies of hydration for all the An^{VI} species studied in Table 8, although both GGA and hybrid DFT calculations predict the values to be more negative than the experimental ones, better agreement is given by the pure GGA PBE calculations, and the hybrid B3LYP functional now shows significant overbinding. For the An^{V} species, however, the GGA results seem to show some underbinding: if our assumption is correct that the "experimental" ΔS_{298}^{hydr} for them falls between zero and −78.6 cal/(mol·K), the values, for example, for uranyl(V) should be between −146.0 and −169.5 kcal/mol, which is closer to the B3LYP results than to the ones given by PBE.

We should remark that changes in selection of the size and shape of the cavity (by choosing different schemes of constructing the surface or choosing different radii) can affect calculated hydration energies quite significantly.[4]

References and Notes

(1) Gibson, J. K.; Haire, R. G.; Santos, M.; Marçalo, J.; de Matos, A. P. *J. Phys. Chem. A* **2005**, *109*, 2768.

(2) Marcus, Y. *Inorg. Nucl. Chem.* **1975**, *37*, 493.

(3) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985.

(4) Gutowski, K. E.; Dixon, D. A. *J. Phys. Chem. A* **2006**, *110*, 8840.

TABLE 8: Gibbs Free Energies of Hydration (Eq 4) and Contributions Thereof, G03 SC-ECP-B3LYP and (in Parentheses) Priroda DZP Four-Component PBE Calculations[a]

	calculated				experimental		
	ΔG_{298} gas phase	$\Delta\Delta G^{solv}$ [b]	ΔG_{298}^{hydr}	ΔG_{298}^{hydr} corrected	ΔH^{hydr} [c]	ΔS^{hydr} [d]	ΔG_{298}^{hydr} [d]
UO_2^{2+}	−224.9 (−192.1)	−167.7 (−169.8)	−392.0 (−361.9)	−413.5 (−383.4)	−397.9	−78.6	−374.5
UO_2^{1+}	−106.0 (−68.5)	−43.7 (−47.5)	−149.7 (−116.0)	−171.2 (−137.4)	−169.5	0.0	−169.5
NpO_2^{2+}	−223.2 (−187.3)	−168.0 (−171.0)	−391.1 (−358.2)	−412.6 (−379.7)	−399.1	−78.6	−375.7
NpO_2^{+}	−113.0 (−64.0)	−41.1 (−45.7)	−154.1 (−109.7)	−175.6 (−131.2)	−180.2	0.0	−180.2
PuO_2^{2+}	−220.1 (−183.8)	−167.8 (−171.5)	−387.9 (−355.3)	−409.4 (−376.8)	−399.4	−78.6	−375.9
PuO_2^{+}	−105.0 (−62.6)	−41.8 (−43.9)	−146.8 (−106.5)	−168.3 (−128.0)	−178.3	0.0	−178.3

[a] Energies in kcal/mol; entropies in cal/(mol·K). [b] CPCM continuum solvation model. For Priroda calculations, $\Delta\Delta G^{solv}$ from Gaussian calculations applied. Definition of $\Delta\Delta G^{solv}$ and ΔG_{298}^{hydr} as in footnotes to Table 7 of the original article. [c] Reference 1. [d] Estimate; based on data from refs 2 and 3 for UO_2^{2+} ; we assume that the entropy of solvation is the same for the neptunyls and plutonyls.

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