Estimating the Gibbs Hydration Energies of Actinium and Trans-Plutonium Actinides

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The use of actinides for medical, scientific and technological purposes has gained momentum in the recent years. This creates a need to understand their interactions with biomolecules, both at the interface and as they become complexed. Calculation of the Gibbs binding energies of the ions to biomolecules, i.e., the Gibbs energy change associated with a transfer of an ion from the water phase to its binding site, could help to understand the actinides' toxicities and to design agents that bind them with high affinities. To this end, there is a need to obtain accurate reference values for actinide hydration, that for most actinides are not available from experiment. In this study, a set of ionic radii is developed that enables future calculations of binding energies for Pu^{3+} and five actinides with renewed scientific and technological interest: Ac^{3+}, Am^{3+}, Cm^{3+}, Bk^{3+} and Cf^{3+}. Reference hydration energies were calculated using quantum chemistry and ion solvation theory and agree well for all ions except Ac^{3+}, where ion solvation theory seems to underestimate the magnitude of the Gibbs hydration energy. The set of radii and reference energies that are presented here provide means to calculate binding energies for actinides and biomolecules.

Introduction

Residing at the bottom of the periodic table, the actinides (An) are a group of radioactive elements that includes uranium, neptunium and plutonium, as well as less known elements that are nevertheless interesting (and occasionally useful). Actinium, americium, curium, californium and berkelium form stable triply charged cations that can interact with macromolecules. Perhaps the most interesting potential application is that of ^{225}Ac as a therapeutic agent for cancer, as this artificial element has favourable properties (half-life duration, decay profile) that make it ideal for targeting tumours locally.[1] To this end, ^{225}Ac should be incorporated into a protein that targets the relevant cancer cell, such as an antibody. Interest in ions of heavier actinides and in particular of the transplutonium elements Am, Cm, Cf and Bk stems from a need to understand their potential toxicity and (for the more common Am and Cm) environmental effects.[2] For this reason, it is crucial to study how such ions can be incorporated into the cells of human and other organisms. Interactions of An with chemical and biological interfaces is also of interest. For example, colloids have a potential to be used for decontamination of radioactive waste.[3] Negatively charged biological interfaces[4–10] that bind cations with high enough affinity might be used in the same vein. The discovery that lanthanide (Ln) ions play a role in the biology of some microorganisms[11] and are used as cofactors in proteins[12] has further added to the interest in An-protein interactions, since Ln and An share many similarities. Moreover, different microorganisms have the potential to interact with An,[13] which can have both positive (detoxification) and negative consequences (environmental accumulation).

Despite the renewed interest in An and in transplutonium actinides in particular, much is not known about these metals and their ions.[14] It is difficult to work with An experimentally as they are radioactive, difficult to separate, difficult to analyse and, with few exceptions, highly difficult to obtain. Computational studies are also challenging due to shortage of experimental references for comparison, the ions' ability to polarise their environment, lack of reliable forcefield parameters for studies with molecular mechanics (MM) potentials and the need to consider relativity in quantum mechanical (QM) studies. Nevertheless, numerous theoretical studies of these ions have been performed,[15–19] as these do not require any amount of rare, radioactive metals or salts.

Any account for interactions between an ion and an interface in an aqueous environment should be studied with reference to the hydrated ion. For this reason, it is of utmost importance to estimate the hydration energy, which is referred to here as the Gibbs energy associated with the transfer of an ion from the gas phase to the aqueous milieu (of note, different terms are used in the literature, including "hydration energy", "Gibbs' hydration energy", "hydration enthalpy" and "solvation energy"; these often but not always refer to exactly the same thermodynamic property). The binding of an ion to a protein, a nucleic acid, a lipid membrane, or any other biological interface necessitates the loss of the ion's hydration shell (at least partially).[10] An^{3+} ions are strongly hydrated,[20] with large (in absolute values) hydration energies and hence in analogy with Ln^{3+} ions[21] do not bind just a random interface, even a polar one. To predict if such ions would bind somewhere, or if they

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ChemPhysChem

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doi.org/10.1002/cphc.202200516

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could replace other ions in their binding site, there is a need to consider the ions' hydration energies as well. Experimental values for hydration energies are often deduced by considering the hydration of various salts. However, for the ions in question here these are not available and must be estimated from theoretical considerations.

The aim of this study was to provide a robust estimation for the hydration energies of Ac^{3+}, Am^{3+}, Cm^{3+}, Bk^{3+} and Cf^{3+} by using a continuum solvation approach. Although fairly rare and difficult to study, these ions have medical, scientific and other uses (e.g., small amounts of Am^{3+} are used in domestic smoke detectors). Predictions made on these ions can eventually be studied also by experiment. The approach can be extended to study heavier An^{3+} ions, but these have very limited use at present.

Theory

Ion Hydration

The hydration energy of an ion refers to the transfer of an ion from the gas phase to an aqueous solution:

$$M^{m+}(g) \xrightarrow{H_2O} M^{m+}(aq) \qquad (1)$$

The standard hydration energy is the standard Gibbs energy change associated with this process. Since the left-hand side is in the gas phase and the right-hand side is in solvent, the standard states are not the same. If we use a theoretical or computational approach to calculate the energy, we have:

$$\Delta G^{hyd} = \Delta G^{calc} + \Delta G^0_{corr} \qquad (2)$$

where ΔG^{calc} is the value estimated by the theoretical approach and ΔG^0_{corr} is a correction for the standard, which is:[22]

$$\Delta G^0_{corr} = RT \ln (V^0/V) \qquad (3)$$

For one mol of perfect gas at $T = 298.15$ K the correction becomes $\Delta G^0_{corr} = 1.89$ kcal mol^{-1}. This value is much smaller than the hydration energies of monoatomic ions and is often not considered in models of ion solvation.

Accounting for Hydration Energies in QM Calculations

Since the cost of studying the solvated state of molecules in room temperature by QM calculations is prohibitive, solvation is often estimated by a continuum approach. The widely used SMD model[23] adopts a universal approach, utilises few parameters, and handles many different solvents. In SMD, a solute cavity is formed by superposition of nuclear-centred spheres. For a monoatomic ion, a single sphere is used. Two sets of radii are used in SMD, one for the calculation of the electronic polarisation energy ΔG_{EP} and one for the calculation of the ΔG_{CDS} term, which stands for cavitation (C), dispersion (D) and local solvent structure (S). Entropy is not considered explicitly but is implicitly incorporated in these two terms.

For most atoms, a single value is used to estimate both ΔG_{EP} and ΔG_{CDS}, termed here r_{SMD} (for the CDS term, the radii are augmented by a constant factor of 0.4 Å). These radii are taken to be the van der Walls (vdW) radii of the atoms using tabulated values (or default values for atoms which were not tabulated). As an example, in the widely used, open source software NWCHEM,[24] these are taken from[25] (only hydrogen) and[26] (all other atoms). Other software use similar set of radii.

Excess optimisation of the Coulomb radii, r_{Coul} (for ΔG_{EP}) was only performed for ten selected atoms. The use of the default vdW radii did not work well for lanthanide ions and in general cannot be expected to be accurate for multicharged monoatomic ions[21] (see for example the values in Table 1). In fact, using the default radii always underestimated the magnitude of the Gibbs hydration energies when calculated by SMD. Instead, the radii should be optimised or estimated somehow. Given a good description of the solvent and ionic radius, the solvation energy could be estimated by using a QM method. ΔG_{EP} thus depends on the QM method to some degree, but mostly on the ionic radius and charge.

Table 1. Hydration energies for selected Ln^{3+} and Pu^{3+}, calculated with SMD using the default radii in NWCHEM version 7.0.2 ($\Delta G^{SMD,1}$) and using optimised radii to reproduce experimental values ($\Delta G^{SMD,2}$). The experimental reference is taken from Ref. [27], but shifted by -11.6 kcal mol^{-1} to account for the difference between the Gibbs hydration energy of the proton as used by Marcus (-252.4 kcal mol^{-1}) and the one that was estimated later from cluster-ion solvation data (-264.0 kcal mol^{-1}).[28] There are small deviations with respect to the values from Ref. [21]; these are due to the use of shifted reference values here whereas in Ref. [21], the values from Ref. [27], were used without modification.

Ion	Default radius (Å)	$\Delta G^{SMD,1}$	Optimised radius	$\Delta G^{SMD,2}$	ΔG^{hyd} (reference)
La^{3+}	2.40	−614.7	1.934	−763.5	−763.3
Nd^{3+}	2.29	−644.2	1.856	−795.5	−795.5
Pm^{3+}	2.36	−625.1	1.847	−799.4	−799.1*
Sm^{3+}	2.29	−644.1	1.831	−806.4	−806.3
Gd^{3+}	2.37	−622.5	1.804	−818.4	−818.2
Dy^{3+}	2.29	−644.3	1.779	−830.1	−830.2
Lu^{3+}	2.21	−667.5	1.733	−851.6	−851.7
Pu^{3+}	2.43	−607.2	1.882	−785.0	−784.8

*Using the calculated value in Ref. [27].

Direct Calculation of Hydration Energies from Ionic Radii

Marcus developed a theory to explain trends in the thermodynamics of ion hydration. Neglecting ΔG_{corr}^0, hydration energies are calculated as:[27]

$$\Delta G^{calc,m} = \Delta G^{el1+2} + \Delta G^{neut} + \Delta G^{asym} \quad (4)$$

In the following, we refer to hydration energies calculated by this theory as $\Delta G^{calc,m}$.

According to Eq. 4, the hydration energy has contributions from:

1. Electrostatic interactions with the first hydration shell water (ΔG^{el1}) and with water molecules beyond the first shell (ΔG^{el2}), which will depend on the ionic radius and the thickness of the shell. Together, these give rise to the ΔG^{el1+2} term.
2. Non-electrostatic interactions due to reorganisation of the water around the ion, ΔG^{neut}.
3. A term that corrects for the asymmetry of the water organisation around cations and anions, where oxygen atoms are closer than hydrogen atoms to a solvated cation and vice-versa for an anion, ΔG^{asym}.

Once again, this description does not take entropy into account explicitly. Instead, the terms in Eq. 4 implicitly include enthalpic and entropic contributions.

Given radii in nm, the terms in Eq. 4 are calculated as follows:

$$\Delta G^{el1+2} = -64.5z^2 \frac{0.44\,(\Delta r/r) + 0.987}{r + \Delta r} \quad (5)$$

z is the ion charge, r is the radius of the hydrated ion and Δr is the thickness of the water shell, which is estimated as:

$$\Delta r = \sqrt[3]{\frac{Az\,d^3}{r\,8} + r^3} - r \quad (6)$$

$A = 0.36$ nm and $d = 0.276$ nm are constants, the first is obtained emprically and the latter represents the diameter of a water molecule. ΔG^{neut} is a function of ion size but not charge:

$$\Delta G^{neut} = 41 - 87r + 1200r^2 \quad (7)$$

Finally, the asymmetry term is simply:

$$\Delta G^{asym} = 120rz^3 \quad (8)$$

Using these equations and constants, Eq. 4 estimates the hydration energy in kJ mol^{-1}. The values were converted here to kcal mol^{-1} and shifted by -11.6 (for the proton hydration term, as in Table 1), for the sake of consistency.

It is obvious that this treatment relies on a prior estimation of the ionic radius. For ions that form complexes with varying number of atoms in the first coordination shell, the ionic radius will depend on the size of the shell: the larger the shell the larger the ion size. Marcus seems to have used data from coordinations with the smallest shell, although this is not mentioned explicitly. The treatment works quite well for Ln^{3+} ions, especially for lighter Ln (Table 2).

Correlation of Ion-O Distances to the Hydration Energies

For ionic species, such as An, where the ionic radii are not known, these must be estimated prior to using SMD or solvation theory. In principle, it is possible to estimate these by simulating ions in solutions, preferably with ab-initio molecular dynamics (AIMD). Such calculations, however, are very demanding and difficult to carry out with sufficient sampling. As an alternative, it is possible to use average ion-O distances in static structures obtained from QM calculations in the gas-phase as a proxy to develop an empirical relation between the solvated ion radius r and the ion-water-oxygen distance d_{M-O}. The underlying assumptions are that r_{SMD} can be approximated as a linear function of d_{M-O}, and that given ions of the same charge and similar chemical properties (Ln^{3+} and An^{3+}) the relation can be extrapolated from one series to the other. In the Results section, it is shown that d_{M-O} is indeed correlated to r_{SMD} of selected Ln. Using the same relation, r_{SMD} values were calculated for Ac^{3+}, Am^{3+}, Cm^{3+}, Bk^{3+} and Cf^{3+}, and the hydration energies were estimated for these ions.

Computational Methods

Gibbs energies for the hydration of the ions were calculated using DFT with the M06 functional[29] and the Stuttgart RSC 1997 basis set with effective core potentials (ECP).[30] The solvent was represented

Table 2. Calculated and experimental hydration energies for Ln, from Ref. [27]. Values in kcal mol^{-1}. MUE = mean unsigned error. RMSE = root mean square error. Lighter Ln = La to Gd.

	$\Delta G^{calc,m}$	ΔG^{hyd}
La^{3+}	−750	−763
Ce^{3+}	−774	−776
Pr^{3+}	−780	−787
Nd^{3+}	−793	−796
Sm^{3+}	−806	−806
Eu^{3+}	−812	−815
Gd^{3+}	−819	−818
Tb^{3+}	−834	−824
Dy^{3+}	−841	−830
Ho^{3+}	−848	−841
Er^{3+}	−856	−847
Tm^{3+}	−864	−852
Yb^{3+}	−872	−865
Lu^{3+}	−880	−852
All ions:		
MUE	8.1	
RMSE	10.7	
Lighter Ln:		
MUE	4.1	
RMSE	5.9	

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doi.org/10.1002/cphc.202200516

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by the SMD model.[23] Calculations were performed with NWCHEM,[24] version 7.0.2. Geometry optimisations of hydrated ions were calculated using the same approach and software, with the def2-tzvp basis set for hydrogens and Ln^{3+} (with ECP for Ln) and def2-tzvpd for oxygens.[31] Ionic radii were taken from the Database of Ionic Radii,[32] compiled from Ref. [33].

Reference experimental values are taken from Ref. [27], and shifted by −11.6 (see the legend of Table 1). There is an anomaly in the reference $\Delta_{hyd}G$ value for Pm^{3+} in Ref. [27], where it is less favourable than the corresponding values for the lighter Nd^{3+} and the heavier Sm^{3+}. Given that the hydration energies are correlated to size (the smaller the ion the more negative the energy) and that the size anti-correlates to atomic number (actinide contraction) the calculated value given as $\Delta_{hyd}G_{calc}^{*}$ in Ref. [27] was used for Pm^{3+} instead of the experimental one.

Results

The Ionic Radii of Lanthanides in SMD Calculations are Correlated to Calculated ion-O Distances in Water

r_{SMD} in hydrated complexes of seven Ln^{3+} which were studied before,[21] were plotted as a function of average ion-O distances calculated for $[Ln \cdot H_2O_n]^{3+}$ clusters (Figure 1). Remarkably, a
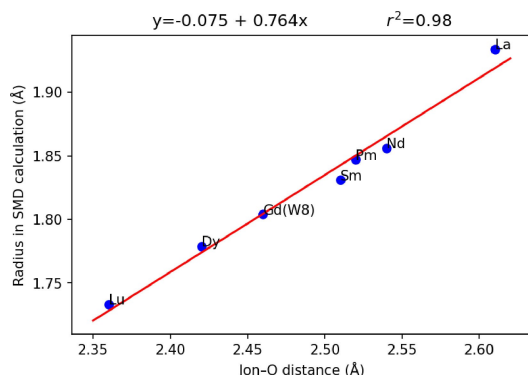

Figure 1. Ion radius in SMD versus calculated ion-O distances in complexes with water. The coordination number was CN=9 for lighter Ln (La to Sm) and 8 for Dy and Lu. Gd can form complexes with CN=8 and CN=9. The CN=8 radius was used here since better correlation is achieved with this CN.

Table 3. Ion-O distances in water, d_{M-O}, from DFT calculations.

Ion	CN	d_{M-O} (Å)
Ac^{3+}	10	2.74
	9	2.70
Pu^{3+}	10	2.60
	9	2.56
Am^{3+}	10	2.59
	9	2.55
Cm^{3+}	10	2.56
	9	2.54
	8	2.50
Bk^{3+}	9	2.53
	8	2.48
Cf^{3+}	9	2.50
	8	2.47

correlation $r=0.98$ was achieved between d_{M-O} and r_{SMD} for these ions.

Ion-O Distances for Ac, Pu and Trans-Plutonium Actinides

Given the scarcity of actinides, less is known on their CNs in water. Average An–O distances calculated with different CN are given in in Table 3. There are multiple estimations for the CN from experimental and theoretical studies, and it is possible that, as is the case for Gd^{3+}, structures with several CN co-exist (for a partial list, see Ref. [34]). In general, the larger is the coordination shell the larger is d_{M-O} (for the same ion), because of repulsion between first-shell waters.

Ac is the lightest An and is often compared to La. Given that even with CN=9 the distance d_{Ac-O} is larger than $d_{La-O}=$ 2.61 Å by almost 0.1 Å, it seems more reasonable to use CN=9 than CN=10 for further calculations. The energy difference for the transformation $[Ac \cdot (H_2O)_9]^{3+} \cdot H_2O \rightarrow [Ac \cdot (H_2O)_{10}]^{3+}$ (a complex with CN=9 and one water in the second hydration shell to a complex with 10 waters in the first shell) was calculated here as $\Delta E = +8.0$ kcal mol^{-1} (in the gas phase). A theoretical study where complexes with CN=4 to 11 has also suggested CN=9 to be the most stable.[35]

Given that Pu, Am and Cm are heavier than Ac and the well known actinide contraction with the increased number of f electrons in the outer shell, CN≤9 should be used for all An heavier than Ac. The choice that was made here was to use CN=9 for Pu, Am and Cm. This would make Am and Cm similar in size to Nd, that is considered as their analogue.[36] The heavier Bk and Cf were modelled with CN=8.

Radii in SMD Calculations and Hydration Energies

Assuming the same relation between d_{M-O} and r_{SMD} as in Figure 1, it is possible to estimate r_{SMD} for An^{3+} and calculate the hydration energies. To this end, r_{SMD} is estimated as:

$$r_{SMD} = -0.075 + 0.764 d_{M-O} \tag{9}$$

The hydration energies were also calculated with the solvation model developed by Marcus (vide supra) based on their ionic radii. The results are presented in Table 4. Estimates made by others using polarisable force fields[37,38] and QM calculations[39] are also presented.

Discussion

Accurate calculations of ion binding energies for multivalent ions are challenging. When precise QM methods are used, system sizes and sampling are limited; conversely, modelling with molecular mechanics is often lacking due to the concentration of charge at one spot and polarisation of the nearby residues.[40–42] To accurately model ion binding at interfaces in complexes,[43] there is a need for a hydrated state as a reference.

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Table 4. Ionic radii (r, CN=6), SMD radii, and calculated hydration energies by DFT (this work, ΔG^{hyd}), Marcus model ($\Delta G^{calc,m}$) and other studies ($\Delta G^{calc,r}$). Radii are in Å, energies in kcal mol^{-1}. The reference value for Pu^{3+} is from Ref. [27], shifted by −11.6 kcal mol^{-1} as explained in the text.

Ion	r	r_{SMD}	ΔG^{hyd}	$\Delta G^{calc,m}$	$\Delta G^{calc,r[37]}$	$\Delta G^{calc,r[38]}$	$\Delta G^{calc,r[39]}$	ΔG^{hyd}_{ref}
Ac^{3+}	1.12	1.988	−743	−713		−721	−733	
Pu^{3+}	1.00	1.881	−785	−780	−839		−780	−785
Am^{3+}	0.98	1.873	−789	−796	−869	−793	−786	
Cm^{3+}	0.97	1.866	−791	−799	−849	−792	−793	
Bk^{3+}	0.96	1.820	−812	−806	−825		−793	
Cf^{3+}	0.95	1.812	−815	−813	−875		−800	

Relying on r_{SMD} values obtained for Ln^{3+} and their correlation to ion-O distances in complexes obtained from DFT calculations, a set of r_{SMD} was obtained for six An^{3+} and their hydration energies were calculated with SMD (Table 4). Among An^{3+}, the data in Ref. [27] lists U^{3+} and Pu^{3+}. U^{3+} ions are not stable in water (they are strongly hydrolysing, and thus UO$_2^{2+}$ (aq) is much more common than U^{3+} (aq)), and were therefore not considered here. An experimental value, ΔG^{hyd}_{ref} is given for Pu^{3+} and is used here for comparison with the calculations. Encouragingly, the calculated value agrees with the experimental one. However, it is noted that observables for Pu^{3+} are difficult to estimate, as other ions (Pu^{4+}, PuO$_2^+$ and PuO$_2^{2+}$) coexist with Pu^{3+} in an aqueous environment. The +4 oxidation is the most common one for Pu, and the +5 state is directly obtained from Pu^{3+} by hydrolysis.

Hydration energies were also calculated by using ion solvation theory. The results of the DFT calculations ΔG^{hyd} and those with ion solvation theory $\Delta G^{calc,m}$ agree to within 2–8 kcal mol^{-1}, about ~1% of the total hydration energies for Pu^{3+} and the trans-plutonium elements. For Ac^{3+}, ion solvation theory underestimated the magnitude of the hydration in comparison with all other methods (Table 4).

In lieu of experimental reference, few studies have applied computational methods to calculate the hydration energies of various An. In one of the first such attempts, a polarisable forcefield was used in molecular dynamics (MD) simulations with the microcanonical NVE ensemble, and systems were studied where a single ion was solvated by 216–1000 water molecules. ΔG^{calc} values were calculated by subtracting the energy of a reference solvent system from that of each ion-containing system and applying corrections to obtain the representative thermodynamic property.[37] The results (Table 4) seem to over-stabilise the solvated ions with respect to the calculations in this study, and do not show the expected trend, i.e., that smaller ions have more favourable hydration energies. Of note, hydration energies of Ln were also calculated in the same study and have shown the correct trend with respect to ion size. Another attempt to obtain the hydration energies of several Ln and An ions with a polarisable forcefield was reported later,[38] this time employing the widely used AMOEBA forcefield and the theoretically robust free energy perturbation (FEP) method, again studying one ion and 215–511 water molecules. In this case, the results were closer to the ones obtained here.

Another reference to the hydration energies was obtained from QM calculations,[39] where the authors calculated the binding of an ion to the first water shell in the gas-phase and corrected for the contribution of the external solvent molecules (by a continuum model), and for the entropy changes associated with formation of the complex in the gas-phase. The use of a continuum model necessitates the definition of atomic radii, but since the authors solvated the hydrated complex the calculations are less sensitive to the radii of the An ions. Remarkably, the results calculated here, ΔG^{hyd} in Table 4, agree well with this more sophisticated treatment (second rightmost column in the same Table), especially for the four lighter An^{3+}. Taking all of the ions into account, the calculated energies agree to within a similar difference (MUE ≈ 9 kcal mol^{-1}) with the previous QM calculations[39] and Marcus' solvation theory.

Conclusions

A set of radii is provided to be used with SMD calculations of complexes with Ac^{3+}, Am^{3+}, Pu^{3+}, Cm^{3+}, Bk^{3+} and Cf^{3+} for calculations of structures or binding energies that could be applied for complexes with biomolecules, molecular interfaces, materials and other molecules. Reference hydration energies agree well with those obtained by the empirical ion solvation theory developed by Marcus and more sophisticated QM calculations. The application of the theory is fairly straightforward and could be expanded to other An^{3+} ions.

Conflict of Interest

The author declares no conflict of interest.

Data Availability Statement

Structures of the hydrated complexes and output files for hydration energy calculations are freely available at: https://doi.org/10.6084/m9.figshare.20653779.v1. Other data will be

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made available from the corresponding author upon reasonable request.

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