

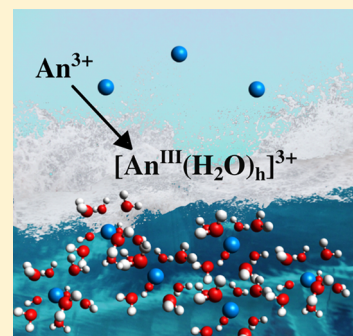
Actinoid(III) Hydration—First Principle Gibbs Energies of Hydration Using High Level Correlation Methods

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S Supporting Information

ABSTRACT: The Gibbs energies of hydration of actinoid(III) ions are evaluated for density functional optimized geometries of $[\text{An}(\text{H}_2\text{O})_h]^{3+}$ complexes ($h = 8, 9$) at the coupled cluster singles, doubles, and perturbative triples level by means of the incremental scheme. Scalar-relativistic 5f-in-core pseudopotentials for actinoids and basis sets of polarized triple- ζ quality were applied. The calculated Gibbs energies for the octa- and nona-aquo complexes agree within 1% with the experimental values which are available only for uranium and plutonium. Compared to the hydrate complexes of the lanthanoid(III) ions those of the actinoid(III) series are slightly less stable.



INTRODUCTION

In the context of nuclear waste disposal, the understanding of chemical processes involving radioactive substances in an aqueous environment is crucial. For instance the residue in the PUREX¹ process (plutonium uranium redox extraction) for separating out uranium and plutonium from spent nuclear fuel contains a variety of radioactive substances in aqueous solution including long lasting minor actinoids like Np, Am, and Cm.² Investigations of their properties in order to gain knowledge about possible mechanisms to separate out additional elements and substances is of major importance—not only for recycling nuclear waste, but also in the context of appropriate disposal of radioactive substances.

Hereby many environmental risks have to be taken into account, e.g. the contamination of surrounding soil and the diffusion of radio active material into groundwater. To develop sufficiently safe and economic storage strategies a profound understanding of environmental processes involving radioactive elements is fundamental.

In this context, we will focus on the hydration of actinoids, since experimental values of hydration enthalpies and free energies are sparse.^{3,4} While the most stable oxidation state of all transplutonium actinoids is +3, this oxidation number can also occur in aqueous solutions of most actinoids⁵ in general. There have been several theoretical studies focusing on the investigation of actinoid(III) hydration enthalpies and free energies.^{6–11} While David and Vokhmin present a thermodynamic model,^{6,12,13} Spezia and co-workers developed a polarizable interaction potential⁸ to predict hydration enthalpies from molecular dynamics simulations.⁹ Wiebke et al. discussed this process in a study based on density functional theory (DFT) using the gradient-corrected BP86 exchange and correlation functionals by Becke¹⁴ and Perdew,¹⁵ respectively, by explicitly treating the An^{3+} ion with a first hydration sphere

consisting of h water molecules ($h = 7, 8, 9$), predicting hydration free energies and preferred hydration numbers of the An^{3+} ions of 8 for the whole actinoid series.⁷ However, in a first wave function-based treatment of the whole actinoid series the same authors obtained coordination numbers of 9 and 8 for Ac^{3+} to Md^{3+} and No^{3+} to Lr^{3+} , respectively, by Möller–Plesset second-order perturbation theory (MP2). DFT calculations using the B3LYP hybrid functional^{16,17} obtained a coordination number of 9 for Cm^{3+} and found the second hydration shell to have significant influence on the first coordination sphere.¹⁸ By means of DFT-based molecular dynamics (MD) simulations it was found that the coordination number of Cm^{3+} also depends on the counteranion.¹⁰ Similar calculations using a different functional found a very flat surface between 8-, 9-, and 10-fold coordinated hydration complexes of Cm^{3+} , with a dynamical water exchange.¹¹ To the best of our knowledge no more rigorous wave function-based correlated investigations of the hydration of all actinoid ions have been published so far. Therefore, we present a quantum chemical ab initio study of An^{3+} hydration at the coupled-cluster level with single, double and perturbative triple excitations (CCSD(T)), covering the whole actinoid series ($\text{An} = \text{Ac}–\text{Lr}$).

In order to obtain experimental coordination numbers, mainly extended X-ray absorption fine-structure spectroscopy (EXAFS) and X-ray spectroscopy have been used. Whereas EXAFS studies on U^{3+} to Cm^{3+} predict slightly higher hydration numbers between 9 and 10, single crystal X-ray structures reveal a trigonal tricapped prism (TTP) structure for the $[\text{M}(\text{H}_2\text{O})_9]^{3+}$ ($\text{M} = \text{Am}, \text{Cm}$) ions, which is also expected to be observed in aqueous solutions.¹⁹ A recent combined EXAFS and MD study of U^{3+} to Cf^{3+} in aqueous solution

Received: August 12, 2014

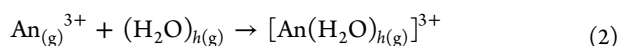
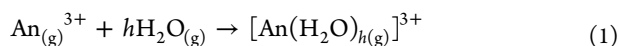
observed in line with the actinoid contraction a decrease of the An–O distance with increasing actinoid nuclear charge, but no change of the hydration number.²⁰ It was concluded that hydration complexes of the actinoid ions up to Cf³⁺ have a 9-fold TTP structure. However, for Cf³⁺, the heaviest aquo-ion observed experimentally so far, a hydration number of 8 was found by an EXAFS study of the aqueous solution coupled with Monte Carlo simulations.²¹ Summing up, although a change of the coordination number from 9 to 8 is expected somewhere near the beginning of the second half of the actinoid series, mainly based on an analogy of the An³⁺ series to the Ln³⁺ series,^{22,23} there is no agreement between experimentalists where precisely it occurs.

Since it has been shown that reasonable ground state structures of open-shell actinoid systems can be obtained using single reference methods, we rely on molecular structures from previous work dealing with An³⁺ hydration at the DFT-level.⁷ In this work only the interaction of the actinoid ion with *h* individual water molecules (*h* = 7, 8, 9) has been calculated, whereas we now provide data on the interaction of An³⁺ ions with water clusters consisting of 8 or 9 water molecules. This model²⁴ has already been applied to Ln³⁺ hydration (Ln = La–Lu) yielding Gibbs energies in very good agreement with experiments.²⁵

Here, we present hydration enthalpies and Gibbs energies of An³⁺ hydration at the CCSD(T) level applying basis sets of triple- ζ quality, taking into account the interaction of trivalent actinoids with 8 or 9 water molecules as well as octa- and non-aqua complexes. Furthermore, we investigate the influence of hydrogen bonding between the [An(H₂O)_{*h*}]³⁺ complexes (*h* = 8, 9) and the surrounding aqueous environment.

COMPUTATIONAL DETAILS

In order to describe the hydration of An³⁺ ions, we first studied the formation of [An(H₂O)_{*h*}]³⁺ with *h* = 8, 9 in the gas phase according to the reaction equations



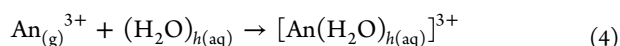
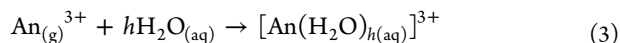
Optimized DFT structures and zero point energies (ZPE) of the actinoid aquo-complexes and H₂O were taken from the work of Wiebke et al.,⁷ the DFT structures and ZPEs of the aqueous species (H₂O)_{*h*} (*h* = 8, 9) from Ciupka et al.²⁵ Gas phase dissociation energies *D*₀ including ZPE corrections are therefore composed of the CCSD(T) binding energy *D*_e and the DFT zero point vibrational energies.

All correlation computations were carried out at the CCSD(T) level using the third-order incremental dual basis-set zero buffer approach (inc3-db-B0)²⁶ and the MOLPRO 2010.1 program package.²⁷ For H and O aug-cc-pVTZ basis sets²⁸ were applied; for An³⁺ energy-consistent 5f-in-core pseudopotentials and corresponding valence-only (7s6p5d)/[5s4p4d] basis sets²⁹ were used unless otherwise noted. The threshold for the correlation energy was set to 10^{−5} a.u.

Regarding the inc3-db-B0 approach, the number of domains *n*_d was set to the number of water molecules in the case of the (H₂O)_{*h*} species and to *h* + 1 in the case of the actinoid complexes to ensure a chemically reasonable distribution of domains based on the structural units of the complexes. For the SCF calculations the basis sets were truncated to s- and p-functions only, whereas for the CCSD(T) calculations the full

basis sets were used. For further information on the dual basis set approach in connection with the incremental scheme please refer to ref 26.

In order to describe the actual hydration, which can be viewed as the transition of a particle from a fixed point in vacuum to a fixed point in solution,^{30,31} we consider



For these reaction equations one can derive hydration energies Δ*E*_H, hydration enthalpies Δ*H*_H and Gibbs energies of hydration Δ*G*_H. Δ*E*_H should here be understood as the ZPE-corrected electronic energy needed for this transfer of an An³⁺ ion and is approximated with

$$\Delta E_{\text{H}} = -D_0 + \Delta E_{\text{SCRF}} \quad (5)$$

where Δ*E*_{SCRF} accounts for the difference in the interaction between the gas phase structures of [An(H₂O)_{*h*}]³⁺ and (H₂O)_{*h*} or *h* H₂O with the aqueous environment. This is modeled by describing the liquid phase with the COSMO self-consistent reaction field (SCRF). Single-point calculations of the gas phase structures within the COSMO SCRF^{32,33} were carried out at the Hartree–Fock level with the previously mentioned basis sets and pseudopotentials using TURBOMOLE version 6.3.³⁴ Actinoid cavity radii were used as determined by Wiebke et al.;⁷ all other parameters were set to default values within the SCRF calculations.

The solvent contribution is then defined by

$$\Delta E_{\text{SCRF}} = (E_{\text{SCRF}}^{[\text{An}(\text{H}_2\text{O})_{h(\text{g})}]^{3+}} - E_{\text{HF}}^{[\text{An}(\text{H}_2\text{O})_{h(\text{g})}]^{3+}}) \quad (6)$$

$$- (E_{\text{SCRF}}^{(\text{H}_2\text{O})_{h(\text{g})}} - E_{\text{HF}}^{(\text{H}_2\text{O})_{h(\text{g})}}) \quad (7)$$

where *E*_{SCRF} is the total energy within COSMO of the superscripted species and *E*_{HF} the corresponding gas phase Hartree–Fock energy, also calculated with TURBOMOLE using the parameters mentioned above.

Gibbs energies of hydration Δ*G*_H were then expressed as

$$\Delta G_{\text{H}} = \Delta H_{\text{H}} - T\Delta S_{\text{H}} \approx \Delta E_{\text{H}} - T\Delta S_{\text{H}} \quad (8)$$

Δ*H*_H had to be approximated by Δ*E*_H, since for An_(g)³⁺ *H*^o data is neither available from experiment nor can it be obtained from quantum chemical calculations. The entropy of hydration Δ*S*_H is substituted by the gas phase entropies Δ*S*^o, because the calculations of thermodynamic properties were carried out on gas phase molecular structures. Furthermore, *T*Δ*S*_H contributions were reevaluated based on the vibrational frequencies⁷ at the DFT level using the module FREEH as implemented in TURBOMOLE version 6.3 applying default parameters for temperature *T* = 289.15 K, pressure *p* = 0.1 MPa, and scaling of wavenumbers with a factor of 0.9914, which was recommended³⁵ for the applied gradient-corrected exchange and correlation BP86 functional.^{14,15} *S*^o_{An³⁺} was approximated by values based on a thermodynamic model.⁶ The hydration entropy was then estimated according to

$$\Delta S_{\text{H}} = \Delta S^{\circ} = S_{[\text{An}(\text{H}_2\text{O})_{h(\text{g})}]^{3+}}^{\circ} - S_{\text{An}^{3+}}^{\circ} - S_{(\text{H}_2\text{O})_{h(\text{g})}}^{\circ} \quad (9)$$

In order to account for the interaction of the explicitly treated first hydration sphere with the aqueous environment more accurately, we defined a correction term depending on the difference Δ*k* of not explicitly treated hydrogen bonds between products and reactants.³⁶ Therefore, we calculated the

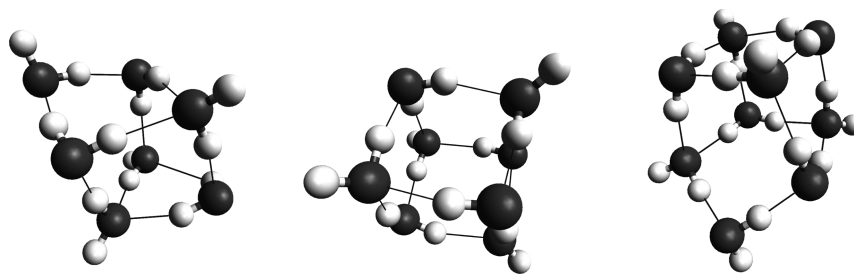
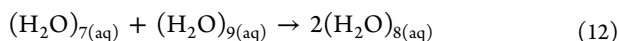
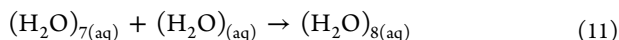
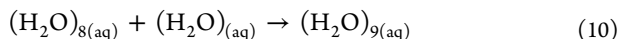


Figure 1. Optimized molecular structures of $(\text{H}_2\text{O})_7$, $(\text{H}_2\text{O})_8$, and $(\text{H}_2\text{O})_9$ clusters.²⁵ Intrinsic hydrogen bonds are marked.

ZPE-corrected, COSMO-SCRF reaction energies of the following reactions:



The energy for the transfer of a water molecule in the aqueous phase into a $(\text{H}_2\text{O})_7$ - or $(\text{H}_2\text{O})_8$ -cluster in the aqueous phase or the transfer of a water molecule from one cluster to another to form the water clusters of interest (Figure 1) should not be dependent on the number of explicitly treated hydrogen bonds when correctly described by the continuum model. Therefore, we expect the reaction energy ΔE^R to be zero.

$$\Delta E^R = \Delta E_{\text{CCSD(T)}}^R + (\Delta E_{\text{COSMO}}^R - \Delta E_{\text{HF}}^R) \quad (13)$$

$\Delta E_{\text{CCSD(T)}}^R$ is the gas phase disassociation energy regarding eqs 10–12, and $(\Delta E_{\text{COSMO}}^R - \Delta E_{\text{HF}}^R)$ is the COSMO contribution at the HF/aug-cc-pVTZ level. From inspection of Figure 1 one can determine $\Delta k = -1$ in eq 10 and 12 and $\Delta k = -2$ in eq 11. An average value for $\Delta E^R/\Delta k$ is obtained as 6.97 kJ/mol. Therefore, we estimate a value for the “explicit hydrogen bond correction” (EHBC) of $\Delta E_{\text{EHBC}} = -6.97 \Delta k$ kJ/mol, i.e.,

$$\Delta H_{\text{H}}^{\text{C,corr}} \approx \Delta E_{\text{H}}^{\text{C,corr}} = \Delta E_{\text{H}}^{\text{C}} + \Delta E_{\text{EHBC}} \quad (14)$$

Finally, as pointed out by Goddard and co-workers, corrections to the standard states for the water molecules and clusters in the thermodynamic cycle have to be added²⁴ (cf. refs 25 and 37 for analogous corrections for the Ln^{3+} hydration). These amount to -12.72 and -12.43 kJ/mol for the 8- and 9-fold coordination, respectively and are included in the final $\Delta G_{\text{H}}^{\text{C}}$ values reported here.

RESULTS AND DISCUSSION

Gas phase disassociation energies, i.e., ZPE corrected gas phase binding energies, of $[\text{An}(\text{H}_2\text{O})_h]^{3+}$ (Figure 2) were calculated according to eqs 1 and 2 (Table 1). The values regarding eq 1 are marked with a superscripted letter “M” (H_2O monomer), values concerning eq 2 with a superscripted letter “C” (H_2O cluster). As expected, the D_0^{M} values agree with the DFT gas phase disassociation energies of previous work,⁷ whereas the D_0^{C} values are significantly lower: the description of the h water molecules as a cluster leads to a stabilization of 226 kJ/mol in the case of $h = 8$ and 254 kJ/mol regarding $h = 9$.

In both cases, the gas phase disassociation energies show a smooth increase with the atomic number Z of the An^{3+} ion, but while D_0 increases by 403 kJ/mol between Ac^{3+} and Lr^{3+} when $h = 8$, it increases only by 384 kJ/mol in the case of $h = 9$. The energy difference between D_0^{C} of $h = 8$ and $h = 9$ decreases

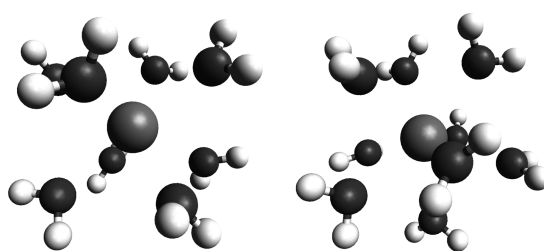


Figure 2. Optimized molecular structures of $[\text{An}(\text{H}_2\text{O})_8]^{3+}$ (left, square antiprism structure) and $[\text{An}(\text{H}_2\text{O})_9]^{3+}$ (right, tricapped trigonal prism coordination).⁷ As an example $[\text{U}(\text{H}_2\text{O})_8]^{3+}$ and $[\text{U}(\text{H}_2\text{O})_9]^{3+}$ are displayed.

therefore from 83 kJ/mol for Ac^{3+} to 64 kJ/mol for Lr^{3+} . The solvent contribution $\Delta E_{\text{SCRF}}^{\text{M}}$ is significantly less negative than the values calculated previously at the DFT level⁷ of theory. In addition there is a difference of 192 kJ/mol ($h = 8$) and 212 kJ/mol ($h = 9$) between the solvent contributions $\Delta E_{\text{SCRF}}^{\text{M}}$ and $\Delta E_{\text{SCRF}}^{\text{C}}$ regarding the monomer and cluster ansatz, respectively.

Hydration energies according to eq 5 are plotted in Figure 3. They follow the general trend of smooth decrease observed in previous first-principles and ab initio studies on An^{3+} and Ln^{3+} hydration.^{7,25,37} However, although the curves approach each other with increasing actinoid atomic number ($\Delta \Delta E_{\text{H}}^{\text{C}} = 33$ and 8 kJ/mol for Ac and Lr, respectively), we do not observe the expected phenomenon of intercrossing energy curves which would point to a change in the preferred hydration number from 9 to 8. Nevertheless, this effect can not only be attributed to a change in energy involving only the treatment of the first hydration sphere. To gain a more detailed understanding on the preferred hydration number, successive hydrogen bond formation and therefore the addition of H_2O molecules into higher hydration spheres might be of interest.

Looking at successive hydrogen bond formation, we find that the interaction between the treated molecule and the surrounding medium is not described with sufficient accuracy by a polarizable continuum model. Therefore, we apply a EHBC term of $-6.97 \Delta k$ kJ/mol as discussed above. Regarding eq 4 for $h = 8$ and 9 the differences in the number of not explicitly treated hydrogen bonds Δk amounts to $\Delta k_8 = 12$ and $\Delta k_9 = 13$, respectively, which is taken into account for the investigation of hydration enthalpies and Gibbs energies of hydration.

Calculated hydration enthalpies and Gibbs energies of hydration are listed in Table 2, where H_{H}^{M} and H_{H}^{C} correspond to $\Delta E_{\text{H}}^{\text{M}}$ and $\Delta E_{\text{H}}^{\text{C}}$, respectively (Figure 3), and $H_{\text{H}}^{\text{C,corr}}$ are the EHBC corrected values. Gibbs energies are evaluated according to eq 8. EHBC corrected enthalpies (Figure 4) and Gibbs energies (Figure 5) also show a smooth decrease and in general

Table 1. Gas Phase Dissoziation Energies D_0 and SCRF Contributions ΔE_{SCRF} of $[\text{An}(\text{H}_2\text{O})_h]^{2+}$ (kJ/mol)

	$h = 8$				$h = 9$			
	D_0^{M}	$\Delta E_{\text{SCRF}}^{\text{M}}$	D_0^{C}	$\Delta E_{\text{SCRF}}^{\text{C}}$	D_0^{M}	$\Delta E_{\text{SCRF}}^{\text{M}}$	D_0^{C}	$\Delta E_{\text{SCRF}}^{\text{C}}$
Ac	1706	-1275	1480	-1467	1817	-1205	1563	-1417
Th	1750	-1291	1523	-1483	1860	-1209	1606	-1421
Pa	1790	-1294	1564	-1487	1900	-1215	1646	-1427
U	1828	-1299	1602	-1491	1938	-1221	1684	-1433
Np	1863	-1304	1637	-1496	1973	-1224	1719	-1437
Pu	1892	-1307	1666	-1499	1999	-1229	1745	-1441
Am	1916	-1311	1690	-1503	2022	-1233	1768	-1445
Cm	1943	-1315	1717	-1507	2047	-1238	1793	-1450
Bk	1967	-1318	1742	-1510	2071	-1241	1816	-1453
Cf	1994	-1322	1769	-1514	2095	-1245	1841	-1457
Es	2018	-1325	1792	-1517	2117	-1248	1863	-1460
Fm	2040	-1328	1814	-1521	2137	-1251	1883	-1464
Md	2065	-1331	1838	-1523	2160	-1253	1906	-1466
No	2087	-1334	1861	-1526	2181	-1257	1920	-1469
Lr	2109	-1337	1883	-1529	2201	-1261	1947	-1473

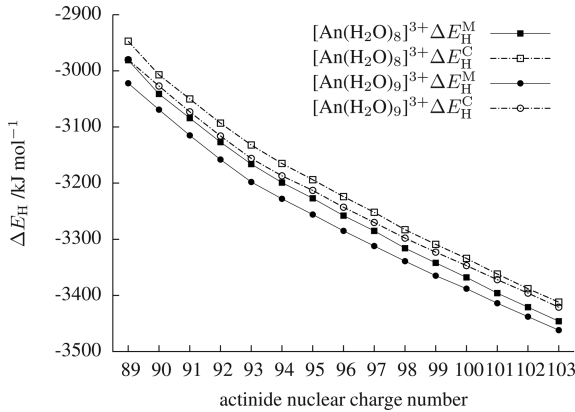


Figure 3. Hydration energies of $[\text{An}(\text{H}_2\text{O})_h]^{3+}$ for $h = 8$ and 9 .

a more moderate slope in comparison to data determined by the thermodynamic model by David and Vokhmin.⁶

The EHBC corrected hydration enthalpies tend to be less negative than the experimental³ values and the enthalpies from

MD simulations⁸ but show a more consistent behavior than the latter. In case of experimental values there are not enough data available to verify certain aspects about trends observed in ΔH_{H} or to discard arguments concerning the behavior of hydration enthalpies on An^{3+} throughout the whole actinoid series.

However, the behavior of lanthanoids(III) and actinoids(III) in aqueous environment is often assumed to be nearly analogous, since many similarities have been found, e.g. the structures of the hydration complexes or the ion water distances. We find the Ln^{3+} hydration complexes to have very slightly higher covalent bonding contributions than the corresponding An^{3+} species (Tables 8 and 9 of the Supporting Information), but also that the noncovalent interaction dominates in both cases. The slightly less ionic character of the lanthanoid complexes is also apparent from the somewhat smaller Mulliken charges on the metal centers (Table 9 of the Supporting Information). In both series one finds for increasing atomic numbers of the central ions increasing covalent contributions, which are accompanied by decreasing Mulliken charges. These increasing covalent contributions are also in line

Table 2. Hydration Enthalpies for the Formation of $[\text{An}(\text{H}_2\text{O})_h]^{3+}$ $h = 8, 9$ According to Equation 3 $\Delta H_{\text{H}}^{\text{M}}$ and Equation 4 $\Delta H_{\text{H}}^{\text{C}}$, the EHBC Corrected Hydration Enthalpy $\Delta H_{\text{H}}^{\text{C,corr}}$ and Gibbs Energy of Hydration $\Delta G_{\text{H}}^{\text{C}}$ According to Equation 8, Calculated from $\Delta H_{\text{H}}^{\text{C,corr}}$ and Including Standard State Corrections (kJ/mol)

	$h = 8$				$h = 9$			
	$\Delta H_{\text{H}}^{\text{M}}$	$\Delta H_{\text{H}}^{\text{C}}$	$\Delta H_{\text{H}}^{\text{C,corr}}$	$\Delta G_{\text{H}}^{\text{C}}$	$\Delta H_{\text{H}}^{\text{M}}$	$\Delta H_{\text{H}}^{\text{C}}$	$\Delta H_{\text{H}}^{\text{C,corr}}$	$\Delta G_{\text{H}}^{\text{C}}$
Ac	-2981	-2947	-3031	-3032	-3022	-2980	-3071	-3068
Th	-3041	-3007	-3090	-3085	-3069	-3027	-3118	-3110
Pa	-3084	-3050	-3134	-3127	-3115	-3073	-3164	-3153
U	-3127	-3093	-3177	-3168	-3158	-3116	-3207	-3195
Np	-3166	-3132	-3216	-3206	-3198	-3156	-3247	-3235
Pu	-3199	-3165	-3249	-3239	-3228	-3187	-3277	-3263
Am	-3227	-3194	-3278	-3267	-3256	-3213	-3304	-3288
Cm	-3258	-3224	-3308	-3294	-3285	-3243	-3334	-3317
Bk	-3285	-3252	-3336	-3319	-3312	-3270	-3360	-3340
Cf	-3316	-3283	-3367	-3349	-3339	-3298	-3389	-3367
Es	-3342	-3309	-3392	-3374	-3365	-3323	-3414	-3393
Fm	-3368	-3334	-3417	-3399	-3388	-3347	-3437	-3415
Md	-3396	-3362	-3446	-3425	-3414	-3372	-3463	-3437
No	-3421	-3388	-3471	-3452	-3438	-3395	-3486	-3461
Lr	-3446	-3412	-3496	-3482	-3462	-3421	-3512	-3494

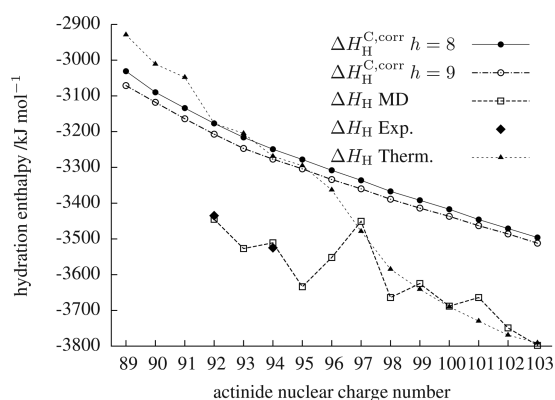


Figure 4. Hydration enthalpies of $[\text{An}(\text{H}_2\text{O})_h]^{3+}$ for $h = 8$ and 9 in comparison to experimental³ reference data (only available for U and Pu) and values calculated using MD simulations⁸ or a thermodynamic model.⁶

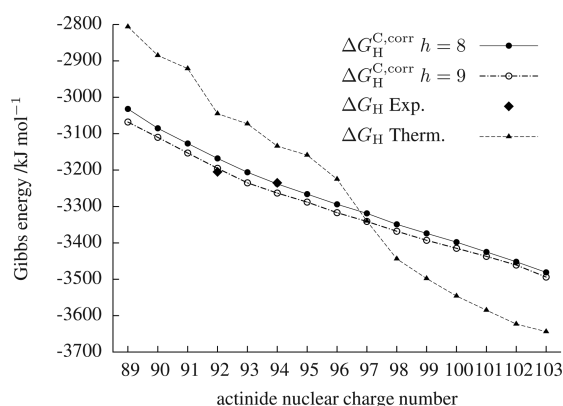


Figure 5. Gibbs energies of $[\text{An}(\text{H}_2\text{O})_h]^{3+}$ for $h = 8$ and 9 in comparison to experimental³ reference data (only available for U and Pu) and values calculated using a thermodynamic model.⁶

with the trend of the calculated hydration energies (Figure 3). An enhanced covalency of actinoid-ligand bonds is sometimes claimed to be the driving force for a preferred extraction of An^{3+} ions by organic ligands such as Cyanex 301.^{38,39} However, besides the covalency of the extraction complexes (products) also the one of the hydration complexes studied here (educts) should be taken into account and alternative explanations be considered.⁴⁰ For a further overview over Ln^{3+} and An^{3+} hydration please see to ref 4.

Our enthalpies mirror as expected the general behavior of experimentally determined enthalpies listed by Marcus³ for the Ln^{3+} series but are significantly less negative, which might be due to the mainly electronic contributions to the enthalpy. The Gibbs energies of hydration show a similar slope with increasing nuclear charge number of the An^{3+} ions and correspond well to the trend expected regarding the experimental ΔG_{H} of the Ln^{3+} series. The calculated ΔG_{H} values for $h = 8$ (U^{3+} -3168 kJ/mol, Pu^{3+} -3239 kJ/mol) and 9 (U^{3+} -3195 kJ/mol, Pu^{3+} -3263 kJ/mol) deviate by at most 1% from the experimentally determined Gibbs energies of U^{3+} (-3205 kJ/mol) and Pu^{3+} (-3235 kJ/mol).³ This is due to the smaller entropy contributions in comparison to the reference hydration entropies, since ΔS_{H} is calculated applying eq 9 using the entropy of the $(\text{H}_2\text{O})_h$ water clusters and not the contribution of h individual water molecules.

Compared to the lanthanoid(III) hydration complexes³⁷ the actinoid(III) species turn out to be by ≈ 70 – 140 kJ/mol ($h = 8$) and ≈ 60 – 120 kJ/mol ($h = 9$) less stable. The differences become smaller with increasing nuclear charges. Whereas in the case of the smaller Ln^{3+} ions, octa- and nona-aquo complexes have very similar Gibbs energies of hydration and a coordination number change is calculated between Er^{3+} and Tm^{3+} ,³⁷ the nona-aquo complexes are slightly favored for all An^{3+} ions (i.e., by 36 kJ/mol for Ac^{3+} and 12 kJ/mol for Lr^{3+}) when using the present computational model.

CONCLUSION

In this study we presented a first principles approach to An^{3+} hydration at the CCSD(T)/TZVP level of theory. We predicted accurate gas phase dissociation energies based on molecular structures optimized at the DFT level, as well as approximate hydration energies and enthalpies of hydration. In addition to previous first-principles studies on the hydration of the Ln^{3+} and An^{3+} series, we do not only take into account the solvent contribution by applying a polarizable continuum model but also introduce an explicit hydrogen bond correction (EHBC) term to model successive hydrogen bond formation to the surrounding aqueous environment. Whereas the calculated corrected hydration enthalpies $\Delta H_{\text{H}}^{\text{C,corr}}$ show the expected smooth decrease but are significantly less negative than the reference data, the Gibbs energies of hydration are located in the same energy range as the experimental values.

Further improvement could be achieved by a geometry optimization within the COSMO approach or a reevaluation of the molecular structures at the CCSD(T) level, which, however, is computationally too demanding with the currently available resources. Furthermore, an explicit treatment of the second hydration sphere as considered by Yang and Bursten¹⁸ could be helpful for further confirmation.

Our results do not mirror the change of the preferred hydration number from 9 to 8, which is assumed due to possible analogies to the lanthanoid series. In this case, it could be beneficial to account for successive hydrogen bonding not only by the EHBC term, but by the explicit simulation of the transfer of a water molecule from the second to the first hydration sphere, which is not part of this work due to the high computational effort at the chosen level of theory. Still, the calculated Gibbs energies of hydration hint to an energetically more favored formation of $[\text{An}(\text{H}_2\text{O})_9]^{3+}$.

Despite the underlying approximations, our model yields reasonable Gibbs energies of hydration which show a smooth decrease with increasing nuclear charge number of the An^{3+} ions. A more detailed description of An^{3+} hydration or in general the hydration of open shell heavy metal ions with high coordination numbers at a more rigorous theoretical level still remains a challenging scientific task.

ASSOCIATED CONTENT

Supporting Information

Calculated energies, enthalpies, and entropies relevant for the evaluation of Gibbs energies as well as covalent and noncovalent contributions to the interaction energy of $[\text{An}(\text{H}_2\text{O})_h]^{3+}$ are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The support of the Deutsche Forschungsgemeinschaft (DFG) for N.H. is gratefully acknowledged.

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