Thermodynamic properties of some tri- and tetravalent actinide aquo ions

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The hydration model that we proposed earlier has been extended to aquo species with covalent bonds. It has been applied successfully to the majority of monatomic ions with charges from −1 to +4. An evaluation of the permittivity in the vicinity of the ion, dipole and quadrupole moments and polarisability of the solvated water molecule is presented. In the case of trivalent and tetravalent actinides, the experimental cation–oxygen distance d, accurately measured by EXAFS, is shorter at the beginning of the series than the calculated values obtained in the ionic model. The observed decrease has been used to evaluate the effective charges, Z_{eff}, of actinides. We discuss the evaluation of the ionic radius R_i, the coordination number N and the number of water molecules in a second hydration shell H. After defining the different parameters, which characterize the aquo ions, mainly, Z_{eff}, R_i, N, H and d, the general hydration and entropy models is applied to evaluate the hydration energy and the entropy of different trivalent and tetravalent actinide aquo ions. We will also re-evaluate and discuss redox potentials corresponding to some 4+/3+ couples. Finally, we will define the radius of the aquo ions and deduce the ionic conductivity of trivalent and tetravalent actinides.

Introduction

Actinides receive constant theoretical interest as a particular group of elements with unusual and rather complicated properties. There is also a practical reason related to involvement of some actinides in nuclear energy cycles, as well as to separation and storage of radioactive wastes. There are several basic reviews[1–4] concerning actinide properties. More specific books have been devoted to particular elements: uranium,[5] americium,[6] neptunium and plutonium.[7] Two main facts have to be underlined. First, for the 5f series many basic characteristics are still not determined because of experimental difficulties, due to high radioactivity. For example, the ionisation potentials and thermodynamic properties, such as entropies, of almost all ions, were only estimated. A second fact concerns the complexity of chemical properties of these elements: existence of a large number of oxidation states, 5f shell contraction and occurrence of relativistic effects. Furthermore, experimental study of the heaviest actinides are handicapped by high instability, as well as low accessibility of these elements.

For a better understanding of actinide basic thermodynamic properties it is a constant challenge to build models that are able not only to reproduce the available experimental data, but also to produce reliable predictions. More generally, it is tempting to establish models which could predict basic chemical properties of any ion in solution, and which are verified by taking into account the large body of available experimental data.

Preliminary attempts[8–11] to calculate actinide thermodynamic properties were based on simple equations with adjustable parameters. However, when parameters have no physical sense, usefulness of such approaches for prediction of actinide properties is doubtful. We have also to stress that one cannot expect reliable evaluation of properties of ions in solutions without taking into account the influence of the electrostatic field in the vicinity of the ions.

Previous calculations of hydration Gibbs energies ΔG_{hyd} were based on the well known Born approximation considering ΔG_{hyd} as the sum of the work done in discharging a sphere with a certain radius and charge in vacuum and charging it again in solvent. Since such a simple scheme ignores many important interactions it leads to poor results.

Another possible way to calculate ΔG_{hyd} is the use of the Molecular Dynamics approach which has been widely developed in recent years owing to the increasing power of computer simulations. Molecular Dynamics considers a chemical reaction as movements of interacting atoms in dynamically changing force fields of molecules, which they compose. It is based on the Born–Oppenheimer approximation and uses the laws of classical mechanics. The most obvious limitation of the method is the use of classical forces, which are realistic only in the case when model interatomic forces are similar to those of real atoms. Obviously, this is not always true. Introduction of quantum mechanical laws could improve the method, but up to now, such an approach has not succeeded in obtaining simulations that fit accurately the experimental data. Therefore, we will not analyze in this article the increasing research linked to these theoretical methods.

So, at the present stage, the most practical and reliable way could be an approach similar to that of Born, but taking into account additional interactions, from a more realistic basis, which appear in the hydration process.

The model

We have proposed a model[12,13] for calculation of hydrated ion thermodynamic properties which takes into account all basic interactions between an ion and surrounding water molecules. As has been shown,[13] it can be applied to either ionic or

† Valery Vokhmin died the 26th of June, 2003.

covalent species. The expression for hydration Gibbs energy is discussed in the cited papers. It includes five basic characteristics of the aquo ions: ionic radius R_i, based on the coherent system of crystallographic radii proposed by Shannon,[14] the coordination number N, the cation–oxygen distance d, which represents the sum $R_i + R_{w1}$, with R_{w1} corresponding to the mean radius of the water molecule in the primary hydration sphere, the number H of water molecules in the second hydration shell and the effective charge Z_{eff} of a cation. It depends also on properties of the water molecules in the vicinity of a central ion: dipole μ and quadrupole θ moments, polarisability α, and permittivity ε of the medium. The equation[12,13] for hydration Gibbs energy $\triangle G^{\circ}$(hyd) contains 7 parameters, P_i, which characterize the "weights" of different interactions, but only the four first play an important role. Each of them is directly expressed through universal physical constants and characteristics of water molecules surrounding an ion. The free hydration energy expression is following:

$$\begin{aligned}\triangle G(\text{hyd}) = {} & P_1 Z_{eff}^2 (R_i + 2\ R_{w1})^{-1} \\ & + P_2\ F_\mu \mid Z_{eff} \mid N(R_i + R_{w1})^{-2} \\ & + P_3\ F_\theta Z_{eff}\ N(R_i + R_{w1})^{-3} \\ & + P_4\ F_\alpha Z_{eff}^2\ N(R_i + R_{w1})^{-4} \\ & + P_5\ H + P_6(R_i + R_{w1})^3 \\ & + P_7\ N\alpha_i/[(R_i + R_{w1})^6(\alpha_w/\chi_w + \alpha_i/\chi_i)] \quad (1)\end{aligned}$$

and for f ions it is necessary to add the nephelauxetic term $P_8 = \delta E^1$.

In the previous papers,[12,13] we have shown that the consideration of (i) experimental determination of d, (ii) the calculation of an "ionic" radius of the water molecule taking into account electrostriction phenomenon, (iii) experimental data of $\triangle G$(hyd) data for lanthanides and (iiii) the expression 1, gives the possibility of evaluating the effective charge of trivalent lanthanides and deducing a simple relation between the observed decrease of the distance, $\triangle d$, and the decrease of the charge, $\triangle Z_{eff}$, when ionic and covalent species are compared.

In the case of hydration entropy and the entropy of the aquo ions,[13] six essential parameters are used: derivatives *versus* temperature of d, N, ε, μ, θ and the energy of ion interaction with the second hydration shell.

In the present work we have slightly changed the thermodynamic data used for parameter calculations. Previously, to evaluate the absolute values of Gibbs hydration energies the value $\Delta G^0(H^+) = -1056$ kJ mol^{-1} was used. Now we prefer to use $\Delta H^0(H^+) = -1096$ kJ mol^{-1}, since the enthalpy value of proton hydration is obtained with higher precision than the corresponding Gibbs energy. The recalculated values of ΔG^0(hyd), which agree now with those given by Marcus[15] have lead to slightly modified values of parameters. They are presented in Table 1.

As was said above, the electrostatic field of an ion in aqueous solution affects the properties of water molecules in its vicinity. We have taken into account the influence of an ion field on the mean radii of water molecules in the first and second hydration shells[16] R_{w1} and R_{w2} in the framework of electrostriction theory developed by Conway and others.[17]

We have also taken into account the corresponding changes in μ, θ and α by introducing the correction parameters F_μ, $F_\theta$and F_α. Thus, μ is represented by the expression:

$$\mu = \mu_0 \cdot F_\mu \quad (2)$$

where

$$F_\mu = 1 \pm (1.43 - R_{w1})/1.43 \quad (3)$$

Here R_{w1} is the radius of a water molecule in the first hydration shell, affected by electrostriction, and 1.43 Å is the limit of the radius corresponding to absence of electrostriction.[12] The positive and negative signs are attributed to cations and anions correspondingly. So, μ_0 is the asymptotic value achieved when $R_{w1} = 1.43$ Å.

For θ the correction parameter

$$F_\theta = 1 + 2.4253 \cdot (1.43 - R_{w1}) \quad (4)$$

is introduced, obtained on the basis of the geometry parameters of a water molecule and a theoretical expression[18] for an ion–quadrupole interaction. So, θ is represented by the expression:

$$\theta = \theta_0 \cdot F_\theta \quad (5)$$

In the case of the polarisability the expression of F_α is the same as for F_μ.

Using the values of the parameters one can extract the unknown value of permittivity in the vicinity of a hydrated ion, as well as the basic characteristics of the water molecules in the first hydration shell. The values of ε_0, μ_0, θ_0, and α_0 for a water molecule situated in the first hydration shell are given in Table 2. One can see that the calculated values of the characteristics are consistent with what we can expect: strong decrease of ε_0 in agreement with the electrostriction theory, increase of μ_0 and decrease of θ_0 and α_0.

Results and discussion

Characteristics of trivalent and tetravalent actinide aquo ions

Local structure of many actinide aquo ions has been determined recently. We will examine reliability and consistency of the data from different experimental works. Then, using our models, we shall undertake calculations of various properties of actinide aquo ions.

In Table 3 we report the coordination numbers of actinide ions obtained in EXAFS measurements.[21–32] Taking into account the published data we consider the values of N, as well as the experimental ion–oxygen distances d_{exp} and the mean distances d_m. We shall see that more reliable data could be determined on the basis of transport properties,[33,34] which allow the establishment of a systematic for a given series of ions, as well as for a large set of ions with different charges.[13]

In the case of Pu^{4+}, where only one estimated value of d is available, we prefer to use the distance $d = 2.38$ Å, obtained by a parabolic extrapolation of d_m values *vs.* R_i for Th^{4+}, U^{4+} and Np^{4+}, rather than $d = 2.39$ Å, since the latter seems to be incoherent with d_m values of other tetravalent actinides.

We can refine N for actinides applying the method used previously for lanthanides,[12,13] *i.e.* correlating N with equivalent conductivity λ_0, and assuming[31] that for U^{3+} $N = 9$ and for Es^{3+} $N = 8$. The calculated values of N for all trivalent actinides are given in Table 4.

Though EXAFS experimental accuracy of N is ±1, we give here the values with two decimals since in computation N was

Table 1 The values of parameters

P_1/ kJ Å mol^{-1}	P_2/ kJ Å^2 mol^{-1}	P_3/ kJ Å^3 mol^{-1}	P_4/ kJ Å^4 mol^{-1}	P_5/ kJ mol^{-1}	P_6/ kJ (Å^{3}mol)$^{-1}$	P_7/ kJ Å^6 mol^{-1}	P_8/ kJ mol^{-1}
−515.4	−333.8	228.2	−273.4	−42.8	1.7	−104.9	−0.7

Table 2 Calculated and experimental values of solvated water characteristics

	Units	Gas phase (exp.)	Bulk (exp.)	1st shell[c]
ε			78[a]	3.88
μ_o	D	1.83[a]	2.42[b]	4.93
θ_o	10^{-39} C m^2	1.87[a]	—	1.02
α_o	10^{-30}m^3	1.46[a]	—	0.77

[a] ref. 15 p. 95. [b] ref. 18 p. 4. [c] this work.

considered as a continuous variable allowing the depiction of the variation of different properties as functions of N when going from one ion to another.

In the case of tetravalent actinides, for which λ_0 values are unknown, N was calculated on the basis of the systematic, proposed in the previous paper.[13] We have shown that the ratio N_{max}/N, N_{max} being the maximum possible number of water molecules in the first hydration shell (when only geometrical considerations are concerned), varyies monotonously *versus* the charge density D on the first hydration shell. D is defined as Z_{eff} divided by the surface of the first hydration shell.[13] Employing the values of R_i and R_{w1}, deduced from d_m, one can calculate the surface of the first hydration shell, D and N_{max} (see ref. 13). Using a general trend in N_{max}/N variation *vs.* D, and calculating N_{max}, one can establish N values.

Here we propose a more natural function $N(D)$:

$$N_{max}/N = D_{max}/D \quad \text{for } D < D_{max}$$
$$N = N_{max} \quad \text{for } D > D_{max} \qquad (6)$$

where D_{max} is the value of D for which $N_{max}/N = 1$. So, for $D = 0$ one obtains $N = 0$, which corresponds to absence of water molecules in the first hydration shell. For $D = D_{max}$, all places in the first hydration shell are occupied: $N = N_{max}$. For D greater than D_{max} one still has to keep $N = N_{max}$, since there is no place for additional water molecules.

Using calculated values of N_{max}, N and D for 43 ions, including trivalent lanthanides and actinides, we have obtained $D_{max} = 0.336$ C m^{-2}. Simultaneously, evaluation of N by applying eqn. (6), gives mean deviations from the experimental coordination numbers of 5%. For the tetravalent actinides eqn. (6) gives values of D greater than D_{max}, so, we have chosen $N = N_{max}$ for all An^{4+}. The N values are given in Table 4.

One can also derive consistent values of the ionic radii for trivalent ions in solution after establishing functions $R_i = f(N)$, as was shown in a previous paper.[13] For Th^{4+} and U^{4+} the values of R_i are known for, correspondingly, six and five different coordination numbers.[14] They can be represented well

Table 3 Experimental, d_{exp} and mean d_m distances in Å, and experimental values of the coordination number N

	d_{exp}	d_m	N
U^{3+}	2.56[a]	2.56	9(1)
Np^{3+}	2.52[a], 2.48[b]	2.5	9(1)
Pu^{3+}	2.51[a], 2.48[c], 2.48[d] 2.51[e]	2.495	9(1)
Am^{3+}	2.51[a], 2.48[f],	2.495	9(1)
Cm^{3+}	2.45[f]	2.45	9(1)
Cf^{3+}	2.43[a],	2.43	9(1)
Th^{4+}	2.45[g], 2.49[h], 2.45[i], 2.45[j],	2.458	11(1)
U^{4+}	2.42[g], 2.43[i], 2.42[j], 2.42[l]	2.423	11(1)
Np^{4+}	2.37[b], 2.40[e]	2.385	10(1)
Pu^{4+}	2.39[c]	2.38	10(1)

[a] Ref. 21. [b] Ref. 22. [c] Ref. 23. [d] Ref. 24. [e] Ref. 25. [f] Ref. 26. [g] Ref. 27. [h] Ref. 28. [i] Ref. 29. [j] Ref. 30. [k] Ref. 31. [l] Ref. 32.

Table 4 Calculated coordination number N and coefficient values of the polynomial expression of the crystallographic radius R_i(Å) *vs.* N

	N	a_o	a_1	a_2	R_i
Ac^{3+}	9.00	0.5615	0.1104	−0.0029	1.320
(Th^{3+})	9.00	0.5045	0.1154	−0.0032	1.284
(Pa^{3+})	9.00	0.4408	0.1214	−0.0033	1.266
U^{3+}	9.00	0.4753	0.1117	−0.0033	1.213
Np^{3+}	9.00	0.4699	0.1091	−0.0031	1.201
Pu^{3+}	9.00	0.4680	0.1057	−0.0030	1.176
Am^{3+}	9.00	0.4641	0.1042	−0.0029	1.167
Cm^{3+}	8.98	0.4736	0.0983	−0.0026	1.146
Bk^{3+}	8.84	0.4786	0.0932	−0.0023	1.123
Cf^{3+}	8.42	0.4819	0.0897	−0.0021	1.088
Es^{3+}	8.09	0.4904	0.0848	−0.0018	1.059
Fm^{3+}	8.01	0.4962	0.0799	−0.0015	1.040
Md^{3+}	8.00	0.5071	0.0746	−0.0012	1.027
No^{3+}	8.00	0.5148	0.0698	−0.0009	1.016
Lr^{3+}	8.00	0.5216	0.0664	−0.0007	1.008
Th^{4+}	11.00	0.5425	0.0771	−0.0018	1.178
U^{4+}	10.65	0.4548	0.0857	−0.0022	1.126
Np^{4+}	10.20	0.4808	0.07 87	−0.0022	1.060
Pu^{4+}	10.00	0.4748	0.0772	−0.0022	1.033

by a polynomial of order 2:

$$R_i = a_0 + a_1 N + a_2 N^2 \qquad (7)$$

with the coefficients a_0, a_1 and a_2 given in Table 4.

For Np^{4+} and Pu^{4+} the R_i values are given[14,32] only for two coordination numbers, namely 6 and 8. Therefore, for these ions only a simple linear relation can be defined. It may give for $N > 8$ only rough estimations of R_i. However, we can refine the R_i values for Np^{4+} and Pu^{4+} on the basis of those established for U^{4+}. To do this we have calculated the mean corrections $\triangle R_i = R_i(\text{linear}) - R_i(\text{polynom})$ for different N using the coefficients for U^{4+} given in Table 4 and applied them to calculate the corresponding R_i curves for Np^{4+} and Pu^{4+}.

For trivalent actinides similar corrections could be found by taking into account the lanthanide data. For these elements $\triangle R_i$ values corresponding to $N = 9$ are:

$$\triangle R_i(9) = c_0 + c_1 R^*_i(9) + c_2 R^*_i(9)^2, \qquad (8)$$

with $c_0 = -0.3465$, $c_1 = 0.6004$, $c_2 = -0.2528$. When $\triangle R_i(9)$ and $R_i(9)$ are evaluated, it becomes possible to obtain a polynomial expression of R_i as a function of N, taking into account the values of R_i for $N = 6$, 8 and 9. The coefficients a_0, a_1 and a_2 are given in Table 4.

Using the values of d_m and the values of R_i, given in Table 4, we have derived the experimental radii of water molecules in the first hydration shell R_{w1}(exp) shown in Table 5. In the same table we present the corresponding hypothetic values for pure ionic case R_{w1}(ion) obtained on the basis of electrostriction theory and in supposition that the trivalent and tetravalent actinides have the charges 3+ and 4+ correspondingly. To reproduce the values of R_{w1} for all trivalent actinides, including unstable ones, we have used the hyperbolic tangent adjusting of R_{w1}(exp) values, similar to that done elsewhere,[13] for trivalent lanthanides, with the superimposed condition $R_{w1}(\text{adj}) = R_{w1}(\text{ion})$ at the end of the series, corresponding to a pure ionic case. The obtained values of R_{w1}(adj) are shown in Table 5. Since they are deduced from a set of experimental data, they are considered to be more consistent than the individual data derived through EXAFS measurement. One can see that the difference $\triangle R_{w1} = R_{w1}(\text{ion}) - R_{w1}(\text{adj})$ for all An^{3+}, shown in the same table, is positive and decreasing with the atomic number, indicating, as expected, an increase of ionicity to the end of the series, with R_{w1}(ion) and R_{w1}(adj) coinciding for Lr^{3+}.

Table 5 The ionic R_{W1}(ion), experimental R_{W1}(exp) and adjusted R_{W1}(adj) values of first shell water molecule radii and the difference $\triangle R_{w1}$ between covalent, $\triangle R_{w1}$(adj), and ionic data, R_{W1}(ion)

	R_{W1}(ion)/ Å	R_{W1}(exp)/ Å	R_{W1}(adj)/ Å	R_{w1} Å
Ac^{3+}	1.372		1.319	0.053
(Th^{3+})	1.369		1.319	0.050
(Pa^{3+})	1.368		1.319	0.049
U^{3+}	1.363	1.347	1.319	0.044
Np^{3+}	1.362	1.299	1.319	0.043
Pu^{3+}	1.360	1.319	1.319	0.041
Am^{3+}	1.360	1.328	1.319	0.041
Cm^{3+}	1.358	1.304	1.322	0.036
Bk^{3+}	1.357		1.333	0.024
Cf^{3+}	1.355	1.347	1.344	0.011
Es^{3+}	1.353		1.348	0.005
Fm^{3+}	1.351		1.348	0.003
Md^{3+}	1.350		1.348	0.002
No^{3+}	1.349		1.348	0.001
Lr^{3+}	1.348		1.348	0.000
Th^{4+}	1.335	1.285		0.050
U^{4+}	1.329	1.297		0.032
Np^{4+}	1.322	1.327		−0.005
Pu^{4+}	1.318	1.344		−0.026

The degree of covalence/ionicity is reflected in our model by a charge located on an ion with an effective charge Z_{eff}. To obtain the effective charges of An^{3+} we have used a linear equation between the relative values $\triangle Z/Z$(ion) and $\triangle R_{w1}/R_{w1}$(ion), with $\triangle Z$ being the difference between the effective and ionic charges. On the basis obtained earlier for Ln^{3+} we have:

$$\triangle Z/Z(\text{ion}) = 0.0077 + 0.9871\ \triangle R_{w1}/R_{w1}(\text{ion}) \qquad (9)$$

Supposing that the same relation holds also for An^{3+} and An^{4+} (considering similar electronic configuration) we have calculated the values Z_{eff} shown in Table 6.

We illustrate the variation Z_{eff} *vs.* R_i for Ln^{3+} and An^{3+} in Fig. 1. One can see the change in Z_{eff} in the middle of both series showing the transition from covalent to ionic bonding with increasing of atomic number and decreasing of R_i. In Fig. 1, R_i is preferred to the atomic number, since it is the physical parameter which is directly related to the property considered. The same tendency manifests itself also in other actinide and lanthanide properties, such as coordination numbers, partial molar volumes and equivalent conductivity.

Table 6 Effective charge Z_{eff}, number of water molecules in the second hydration shell H, molar refractivity R (in $cm^3\,mol^{-1}$), ratio of the maximum number of possible solvated water molecules, N_{max}, to the coordination number N, charge density on the primary shell D (in $C\,m^{-2}$) and Gibbs hydration energy $\triangle G°$(hyd) (in $kJ\,mol^{-1}$)

	Z_{eff}	H	R	N_{max}/N	D	$G°$(hyd)
Ac^{3+}	2.88	6.99	10.6	1.39	0.2788	−2806
(Th^{3+})	2.88	7.10	10.4	1.36	0.2807	−2885
(Pa^{3+})	2.88	7.16	10.2	1.35	0.2816	−2921
U^{3+}	2.88	7.32	10.0	1.30	0.2843	−3045
Np^{3+}	2.88	7.36	9.8	1.29	0.2850	−3073
Pu^{3+}	2.88	7.45	9.6	1.27	0.2863	−3134
Am^{3+}	2.88	7.49	9.5	1.27	0.2871	−3159
Cm^{3+}	2.89	7.66	9.3	1.25	0.2897	−3225
Bk^{3+}	2.93	8.18	9.1	1.25	0.2980	−3340
Cf^{3+}	2.96	9.22	8.9	1.29	0.3139	−3444
Es^{3+}	2.97	10.00	8.7	1.31	0.3252	−3498
Fm^{3+}	2.97	10.24	8.5	1.31	0.3286	−3546
Md^{3+}	2.97	10.32	8.3	1.30	0.3298	−3585
No^{3+}	2.97	10.38	8.2	1.29	0.3307	−3623
Lr^{3+}	2.97	10.42	8.0	1.28	0.3312	−3644
Th^{4+}	3.82	13.41	9.8	1.00	0.3683	−6100
U^{4+}	3.88	14.33	9.4	1.00	0.3794	−6301
Np^{4+}	3.97	15.68	9.2	1.00	0.3965	−6494
Pu^{4+}	3.97	16.28	9.0	1.00	0.4036	−6444

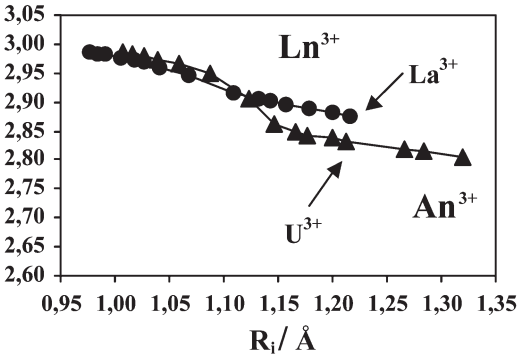

Fig. 1 Variations of the effective charges Z_{eff}. of the trivalent lanthanides and actinides *vs.* R_i.

It is interesting to compare the variations of Z_{eff} in the lanthanide and actinide series. In the Fig. 1 one can see that in the first half of the series the Z_{eff} of actinides is lower, as expected, than that of lanthanides, showing a greater degree of covalence, whereas at the end of both series Z_{eff} is close to the pure ionic value 3+.

For An^{4+} R_{w1}(ion) is greater than R_{w1} for Th^{4+} and U^{4+}, but this is not the case for Np^{4+} and Pu^{4+}. However, the negative value of $\triangle R_{w1}$ for Np^{4+} is, in fact, close to zero. The appreciably negative $\triangle R_{w1}$ value for Pu^{4+}, may be caused by a large error in the d_{exp} value. In any case, one can conclude that for Np^{4+} and Pu^{4+} the bonding should be close to ionic.

Considering this discussion concerning the appearance of a covalent effect at the beginning of the tetravalent actinide series (as well as in the trivalents of lanthanides and actinides) we can understand that ions with large R_i values, and, consequently, small electrostatic field, have larger "ionic" values of the water molecules, R_{w1}(ion). But, simultaneously, covalent effect decreases the experimental distance d_m and the experimental R_{w1} radius values. Therefore, after the calculation of adjusted values, R_{w1}(adj), these quantities and R_{w1}(ion) are varying with R_i in the opposite direction.

Evaluation of the free hydration energy

To obtain $\triangle G°$(hyd) values, the FORTRAN program HYDRA[12,13] computes all basic characteristics of the central ion and water molecules in its vicinity: R_i, N, H, Z_{eff}, R_{w1}, R_{w1}(ion), D and PF (Packing Factor[12,13]). The latter serves as a geometrical correction which allows one to take into account the void spaces between water molecules in the first hydration shell in R_{w1}(ion) calculation.

To calculate H we have used the correlation observed previously[13] between H and D:

$$H = d_0 + d_1 D + d_2 D^2, \qquad (10)$$

where $d_0 = -1.692$, $d_1 = 2.198$ and $d_2 = 103.778$. For PF calculation a similar correlation was applied:

$$PF = e_0 + e_1 D + e_2 D^2, \qquad (11)$$

where $e_0 = 0.6813$, $e_1 = 0.8282$, $e_2 = -1.3837$.

Because different properties depend on each other they are calculated by loops until self-consistency is achieved. Using R_{w1}(ion), calculated by electrostriction procedure, and R_{w1}, obtained as the difference $R_{w1} = d_m - R_i$, the effective charges Z_{eff} are calculated the way discussed above. The values of Z_{eff} are given in Table 6. In order to calculate $\triangle G$(hyd) we have also to evaluate α, α/χ and δE^1.

The two first quantities, corresponding to the dispersion term,[12,13] give small contributions to $\triangle G^{\circ}$(hyd) values (about 1%) and are evaluated similarly to those of the lanthanides.[12,13] Since α is directly proportional to the molar refractivity R, that quantity has been evaluated as for lanthanides[13] and the data are reported in Table 6. The last parameter, characterizing the nephelauxetic effect, is very small and supposed to be independent of an ion. It is obtained exactly as for the lanthanides.[12,13]

That done, we are able to calculate $\triangle G^{\circ}$(hyd) of trivalent and tetravalent actinides by eqn. (1). The obtained values of $\triangle G^{\circ}$(hyd) are given in Table 6.

Entropies of the tri- and tetravalent actinide aqua ions

According to the model proposed in our recent paper,[13] we can evaluate the absolute hydration entropy of monatomic ions with eqn. (12) of ref. 13 (in an absolute scale). These values are reported in Table 7 with the entropies of the gaseous ions obtained by the Sackur Tetrod equation. In the same table we give the entropies of the aquo ions (in a conventional scale, considering[15] $S^{\circ}_{aq}(H^{+}) = -22.2\ J{\cdot}K^{-1}\ mol^{-1}$). The calculated entropy data are compared with the measured and estimated data. The entropy differences δS° between calculated and experimental data[7,36] are also reported in Table 7. For trivalent actinides, the mean deviation between the two sets of data is 9 eu., which is consistent with the 9 eu. difference obtained for the alkalis, alkaline-earths and trivalent lanthanides. For the tetravalent actinides the average difference between the estimated and calculated values is 10 eu. So, all deviations between the experimental and calculated data are consistent with the published uncertainties.

The comparison of the calculated and experimental values of S°_{aq} for ions with charges +1 (alkalis), +2 (alkaline-earths), +3 (lanthanides and actinides) and +4 (Ce^{4+} and tetravalent actinides) as functions of the radius R_i shows an excellent agreement between the two sets of data. For each series of ions the hydration entropies become less negative when R_i. increases. This should be related to the observed increase of the coordination number with R_i.

In contrast, the previous published estimations[36] for U^{4+}, Np^{4+} and Pu^{4+} present an opposite trend and differ essentially from the present data. This discrepancy has been corrected in the last analysis of the entropy data.[7]

Using re-evaluated entropies for actinide ions along with the literature data on the enthalpies of ion formation and metal entropies,[11,36] we can recalculate the formation entropies of aquo ions $\triangle S_f$ (Table 7) and Gibbs formation energies of the aqua ions, as well as standard redox potentials of the 3/0, 4/0 and 4/3 couples. The calculated potentials, reported in Table 7, are consistent with the previously evaluated values, in particular with the experimental standard $E^{\circ}(4/3)$ redox potentials.[7] These conclusions serve as additional verification of the consistency of the models and their applicability to the series of tri- and tetravalent actinides.

Size of the actinide aquo ions and transport properties

Because our determination of the number and size of water molecules was especially based on precise values of transport properties (conductivities and mobilities[13,34]), the HYDRA program, which gives us the possibility of calculating N, H, R_{w1} and R_{w2}, allows, inversely, the evaluation of the radius of the aquo ion (R_2) and its Stokes radius (R_s). R_2 and R_s have been reported in Table 7. Then, application of solution chemistry equations allows calculation of different transport properties. For instance, the equivalent conductivity of an ion at infinite dilution is given by the relation

$$\lambda_0 = 0.820\ Z_{eff}/(R_s\eta_0) \qquad (12)$$

where η_0 is the viscosity of the solution at infinite dilution. The calculated λ_0 data are reported in Table 7 for trivalent and tetravalent actinides. A comparison of the ionic equivalent conductivity of trivalent lanthanides (ref. 16) with the calculated values (this work) for trivalent and tetravalent actinides is presented in Fig. 2. In the same figure we show the calculated ionic equivalent conductivity of trivalent actinides. The values are represented as functions of R_i. One can see that the calculated values of λ_0 for trivalent lanthanides and actinides corresponding to the same value of R_i are rather close to each other. This is due to the fact that for actinides both Z_{eff} and R_s are diminished, which leaves λ_0 approximately unchanged correspondingly with eqn. (11).

Table 7 The calculated hydration entropy $\triangle S$(hyd), the entropies of gaseous ion S° gas and of the aquo ion S°aq, the difference $\delta S^{\circ} = S^{\circ}$aq(pub.) – S°aq (calc), the formation entropy $\triangle S_f$, in J mol^{-1} K^{-1}, the standard redox potentials $E^{\circ}(3/0)$, $E^{\circ}(4/0)$, $E^{\circ}(4/3)$, the calculated radius R_2 of the aquo ion, the Stokes radius $R_s$in Å and equivalent conductivity $\lambda_0$in S cm^2 eq^{-1}, c. and a. indicate conventional and absolute scales respectively

	S(hyd) calc., a.	S°gas calc.	S°aq calc., c.	S°aq exp., c.	δS° calc.	$S_f$calc., c.	$E^{\circ}(3/0)$/ V	$E^{\circ}(4/0)$/ V	$E^{\circ}(4/3)$/ V	R_2/ Å	R_s/ Å	λ_0/ S cm^2 eq^{-1}
Ac^{3+}	−411	176	−168	−180	−12	−33	−2.222			4.52	3.94	67.1
(Th^{3+})	−421	192	−163	0		−20				4.52	3.95	66.9
(Pa^{3+})	−426	195	−164	0		−20				4.53	3.96	66.9
U^{3+}	−441	196	−178	−175	3	−32	−1.656			4.54	3.98	66.7
Np^{3+}	−444	195	−183	−194	−11	−37	−1.783			4.54	3.98	66.7
Pu^{3+}	−451	192	−193	−185	8	−53	−1.991			4.55	3.99	66.6
Am^{3+}	−454	186	−201	−201	0	−59	−2.069			4.55	4.00	66.6
Cm^{3+}	−459	195	−198	−188	10	−74	−2.049			4.56	4.02	66.4
Bk^{3+}	−464	199	−199	−188	11	−81	−1.993			4.59	4.08	66.1
Cf^{3+}	−469	201	−202			−86	−1.905			4.65	4.19	64.9
Es^{3+}	−475	201	−207			−100	−1.973			4.69	4.28	63.8
Fm^{3+}	−479	201	−212			−107	−2.056			4.71	4.31	63.5
Md^{3+}	−483	199	−217			−108	−1.737			4.72	4.33	63.3
No^{3+}	−486	195	−224			−93	−1.258			4.72	4.34	63.2
Lr^{3+}	−489	178	−244			−103	−2.060			4.73	4.34	63.2
Th^{4+}	−703	177	−438	−423	15	−230		−1.815		5.02	4.86	72.7
U^{4+}	−717	195	−433	−414	19	−222		−1.361	−0.473	5.10	4.99	71.8
Np^{4+}	−704	196	−420	−426	−7	−209		−1.280	0.231	5.23	5.18	70.5
Pu^{4+}	−693	195	−409	−415	−6	−204		−1.242	1.007	5.26	5.23	69.9

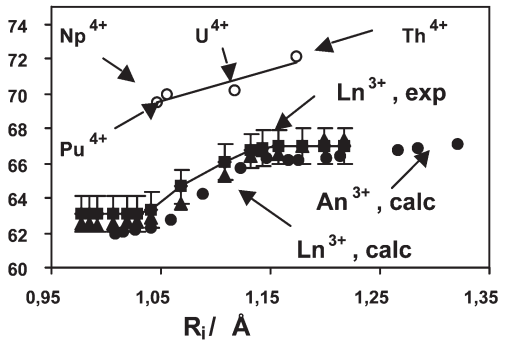

Fig. 2 Variations of the experimental and calculated values of the ionic equivalent conductivities of trivalent lanthanides and calculated data for tri- and tetravalent actinide aquo ions *vs.* ionic radii.

We have also considered the determination of ionic conductivity of tetravalent actinides. In this case, the experimental measurement is practically impossible, and a reliable calculation of this quantity is useful for the nuclear energy industry.

Conclusions

We have shown that the hydration Gibbs energy and entropy models permit us to evaluate and predict with reliability and consistency the main characteristics of the monatomic actinide ions: free hydration energy, hydration entropy and entropy of the aquo ions. They enable us as well to derive for the first time consistent effective charges, coordination numbers, radii and transport properties. The model for $\triangle G^{\circ}$(hyd) also permits the calculation of the distances between the cation and the water molecules situated in the first and second hydration shells in the case of pure ionic species, taking into account the electrostriction effect. So, it can serve as a useful tool to analyze the experimental data obtained by EXAFS. The comparison between experimental and calculated values of Gibbs hydration energies gives a standard deviation of less than 1% (10 to 20 kJ mol^{-1} for lanthanides), which is much smaller than for the results obtained by pure theoretical computations, which give for heavy elements an uncertainty of about 200 kJ·mol^{-1}. For entropies, the standard deviation is less than 5%, which is sufficient for experimental purposes.

Application of our models to 3d, 4d and 5d elements are in progress. We have already shown that our general models and equations could be applied to these elements, with charges 2+, 3+ and 4+, if we take into account the important ligand field effect. Therefore, K Dq, an additional term, which quantifies this effect, has to be introduced. A subsequent article will be devoted to these series of ions.

Finally, we are confident that the proposed models could be developed further, and applied also to polyatomic ions such as uranyl ions with penta- and hexa-oxidation states, which exist in the first half of the actinide series.

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