9704 *J. Phys. Chem. A* **2001,** *105,* 9704−9709

Hydration and Entropy Model for Ionic and Covalent Monatomic Ions

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Received: February 5, 2001; In Final Form: May 21, 2001

The hydration model we had proposed has been extended to aquo species having a covalent bond. In this case, the experimental cation−oxygen distance (δ) is shorter than the calculated data obtained with an ionic model. The observed decrease is used to evaluate the effective charge of the covalent species. We discuss the evaluation of the coordination number (N), the number of water molecules in a second hydration shell (H), and the radius (R_w) of the water molecule in the two hydration shells and give useful expressions for their determinations. Because the hydration entropy and entropy of the aquo ion (S_{aq}) can be deduced from the derivative of the free hydration energy (ΔG(hyd)) versus temperature, we propose an entropy model, considering six terms corresponding to the derivative versus temperature of the distance δ, the number N, the dielectric constant, the dipole and quadrupole moments of the water molecule, and the binding energy of the water molecule in the second hydration sphere. The two proposed models are tested for ions with charges −1, +1, +2, and +3. The calculated ΔG(hyd) and $S°_{aq}$ data are in excellent agreement with available experimental data. We have shown that the models can be extended to tetravalent ions. Finally, according to the relationships between the main characteristics of the aquo ions, we were able to conclude that the characteristics of an aquo ion can be defined to a great extent by two main parameters: the crystallographic radius and the cation−oxygen distance, which are both measured with accuracy by X-ray diffraction and X-ray absorption spectroscopy. Moreover, the consideration of the proposed equations could be used to predict or determine interesting characteristics such as N, q_{eff}, H, or δ.

Introduction

In a recent paper[1] we have proposed a model of an ion in solution, which allows the quantification of the free hydration energy as a sum of eight different terms. They correspond to the main interactions taking place in the electrolyte. The obtained relation is for cations

$$\Delta G(\text{hyd}) = aq^2(R_c + 2R_w)^{-1} + bF|q|N(R_c + R_w)^{-2} + cF^2qN(R_c + R_w)^{-3} + dFq^2N(R_c + R_w)^{-4} + eH + f(R_c + R_w)^3 + gN\alpha_i/[(R_c + R_w)^6(\alpha_w/X_w + \alpha_i/X_i)] + K\delta E^1 \quad (1)$$

and F has to be changed in $1/F$ for anions. It depends on five main parameters: the charge (q) of an ion, the crystallographic radius (R_c), the corresponding coordination number (N), the radius (R_w) of the water molecule in the first hydration shell, and the number (H) of water molecules in the second hydration shell. These are considered as the main characteristics of an aquo ion. The parameter F, as indicated previously,[1] corresponds to the ratio $1.43/R_{w1}$ and is correlated with the polarization of the water molecule in the field of the central ion. Because characteristics such as dielectric constants which are included in the equations with parameters (a, b, etc.) are not precisely known in the vicinity of the ion, relation 1 has been established[1] by considering 27 elements, including 15 lanthanides, which were considered as examples of monovalent, divalent, and trivalent ions. In the first stage, it was assumed that all of the species were purely ionic. The aim of this work is to examine how the model could be applied to covalent species. We will also consider new species, especially tetravalent ions. To simplify the calculation, we will give empirical expressions for some of the essential characteristics, which are deduced from HYDRA1 computations, and avoid the use of this program. A particular discussion will be devoted to the question of the effective charge and the entropy determination.

Crystallographic Radius

The aquo ions exist in solution with coordination numbers N which are generally measured as fractional numbers. So, we assume that, in this medium, statistically different types of structures of the first coordination shell coexist. Because the crystal radius depends on N, it is therefore necessary to evaluate the radius for the given average N value. We have considered the published radii given for several coordination numbers[3,4] and obtained a polynomial expression for each ion:

$$R_c = a_0 + a_1N + a_2N^2 \quad (2)$$

The constants a_0, a_1, and a_2 are reported in Table 1.

Radius of the Water Molecule. The experimental value of the radius of the water molecule in the first hydration shell (R_{w1}) is determined as the difference between the measured hydrated ion−oxygen distance (δ) and R_c. It was observed[1,2] that R_{w1} is not constant, as is usually assumed, but depends on the electrical field existing in the vicinity of the ion. An evaluation of the radius of the water molecule has been achieved by applying the electrostriction theory.[1,2] However, in this case, the macroscopic model considers the volume of the molecule, which includes the void spaces existing in solution between the

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10.1021/jp0104278 CCC: \$20.00

TABLE 1: Constants a_0, a_1, and a_2 of Expression 2 of R_c with N, a_0, a_1, and a_2

	a_0	a_1	a_2		a_0	a_1	a_2
F^-	1.270	0.010	0.000	Pr^{3+}	0.342	0.138	−0.005
Cl^-	1.750	0.010	0.000	Nd^{3+}	0.461	0.105	−0.003
Br^-	1.900	0.010	0.000	Pm^{3+}	0.433	0.111	−0.004
Li^+	0.250	0.085	0.000	Sm^{3+}	0.488	0.092	−0.002
Na^+	0.930	0.015	0.000	Eu^{3+}	0.481	0.091	−0.002
K^+	1.350	0.005	0.000	Gd^{3+}	0.495	0.086	−0.002
Rb^+	1.250	0.045	0.000	Tb^{3+}	0.550	0.065	−0.001
Cs^+	1.460	0.035	0.000	Dy^{3+}	0.543	0.065	−0.001
Mg^{2+}	0.720	0.000	0.000	Ho^{3+}	0.485	0.078	−0.001
Ca^{2+}	1.005	0.000	0.000	Er^{3+}	0.585	0.046	−0.001
Sr^{2+}	1.420	−0.100	0.010	Tm^{3+}	0.554	0.052	0.000
Ba^{2+}	1.380	−0.035	0.005	Yb^{3+}	0.519	0.058	
La^{3+}	0.540	0.096	−0.002	Lu^{3+}	0.465	0.072	−0.001
Ce^{3+}	0.507	0.097	−0.002	Ce^{4+}	0.461	0.079	−0.002

molecules. It corresponds microscopically to a radius $R_{e1} > R_{w1}$. R_{e1}, as well as R_{w1}, depends on the charge, the radius R_c, and the ion−water distance. Therefore, to compare experimental (R_{w1}) and calculated values (R_{e1}), we have to introduce a packing factor (PF), which has been defined[1] as the ratio R_{w1}/R_{e1}. PF has been determined for each ion, and average values have been obtained for halide, alkali, divalent, and trivalent ions.[1] Because the obtained PF values are slightly increasing with the charge and the radius of the hydrated ion, as expected, we can also obtain a more general systematic value by considering that PF should depend on the charge density (D_1) on a sphere with a surface S_1, having the radius $R_c + 2R_{e1}$. D_1 is expressed as

$$D_1 = q/S_1 \tag{3}$$

Using the mean PF values calculated for groups of ions with particular charges and the corresponding mean D_1 values (evaluated in SI units), we have obtained the relation

$$\mathrm{PF} = 0.7348 + 0.0397D - 0.0055D^2 \tag{4}$$

where D corresponds to the D_1 value multiplied by 10. This relation is applied to obtain the PF values for all of the cations (excluding the anions). These data are reported in Table 2.

In the case of tetravalent ions, structural determinations in diluted solutions have been achieved by EXAFS. For Ce^{4+}, a difference equal to 0.08 Å has been evaluated between the ion−oxygen distance for tetravalent and trivalent ions.[5] Because the distance for Ce^{3+} of $\delta = 2.53_9$ Å has been accepted,[1] one obtains $\delta = 2.46$ Å for Ce^{4+}. Using the coefficients in Table 1 for Ce^{4+}, we can obtain the values of R_c for different N. Using these and $\delta = 2.46$ Å, we find that, for $N = 10-12$, the values of R_{w1} are equal to 1.396, 1.357, and 1.322 Å, respectively. The value of R_{w1} for Ce^{4+} should be smaller than that for Ce^{3+}. Because $R_{w1} = 1.333$ Å for Ce^{3+} (see Table 2), one can deduce the coordination number of around 11 for Ce^{4+}. A more precise evaluation of N with the program HYDRA gives $R_{w1} = 1.329$ Å and $N = 11.69$ for Ce^{4+} (see Table 2).

Using the calculated values of R_{w1}, we can simplify the determination of R_{w1} by considering, for each series of ions (charge from −1 to +4), a polynomial expression of R_c:

$$R_{w1} = b_0 + b_1R_c + b_2R_c^{\,2} \tag{5}$$

The parameters b_0, b_1, and b_2 for each series of ions are given in Table 3.

Coordination Number. The coordination number is an essential characteristic of the aquo ion. Because numerous direct measurements of the coordination number N, by neutron and X-ray diffraction methods or EXAFS, show large experimental deviations[6,7] with an experimental accuracy of around one molecule, we will consider more reliable values of N which have been evaluated in our previous paper.[1] The variation of N versus the crystallographic radius R_c has been plotted in Figure 1. In this plot, R_c corresponds to the coordination number considered, and the values of N for monovalent, divalent, and trivalent ions are taken from our previous paper.[1] We have also added, in Figure 2, data for Ce^{4+} and some tetravalent ions, which will be discussed in a future paper.

To analyze and compare the values of N in the different series of ions, we have considered, for the sphere S with the radius shown, that R has the expression

$$R = (R_c^{\,2} + 2R_{e1}R_c)^{0.5} \tag{6}$$

On the surface S, each water molecule occupies the surface s which can be calculated by the equation

$$s = 2\pi R[R - R^2/(R_c + R_{e1})] \tag{7}$$

The surface s is shown in Figure 2 and corresponds to the shaded area.

In accordance with eqs 6 and 7, the maximum number (N_m) of water molecules in the first hydration sphere can be expressed as

$$N_m = S/s = 2/[1 - R/(R_c + R_{e1})]$$

The ratio N_m/N should depend on the charge of the ion. We can expect that, for a high charge on the ion, the number N of water molecules should tend toward the maximum number N_m, so that N_m/N is always higher or equal to 1.

To compare simultaneously all of the ions, from charges +1 to +4, we have considered the variation N_m/N with the charge density D_1. D_1 and D are evaluated as indicated previously. The plot of N_m/N versus D is shown in Figure 3 along with a regression curve of the data

$$N_m/N = 2.3838D^{-0.6439} \tag{8}$$

As expected, a smooth decrease of the N_m/N ratio is observed when D_1 is increasing. For alkalis, the charge and D_1 are small, so the ratio N_m/N is large (i.e., only a part of the surface S is occupied by water molecules). However, the model shows erratic data for Li^+ and Cs^+. The reason for these discrepancies is not yet understood, but it does not contradict the observed trend. In the case of the Ce^{4+} ion, the obtained ratio N_m/N is close to 1 (i.e., the number of coordinated water molecules corresponds to the maximum number N_m). In a next paper, it will be shown that for high charged species such as tetravalent thorium, uranium, neptunium, and plutonium, where experimental values have been published[8−11] ($N \approx 10-11$), the entire surface S is also occupied by water molecules. Because we can evaluate S and s for each ion, the correlation between N_m/N and D_1 gives a possibility to evaluate consistently the ratio for a given D_1 value and, therefore, to calculate N. In particular, because $N_m/N \approx 1$ for tetravalent species, we have accepted N for these ions to be equal to N_m. Such an evaluation is consistent with the experimental data and is reported in Figure 1.

Another possibility to evaluate N is to consider the experimental determination of the distance δ, because $\delta = R_c + R_{w1}$. The last two quantities can be calculated as functions of N as shown in the previous paragraphs, and we have also calculated the distance $\delta_{calc}(N)$ which fits the experimental data. This

TABLE 2: Coordination Number *N*, Ratio of the Maximum Value N_m versus *N* (Eq 6), Packing Factor PF, Charge Density D_1, Effective Charge q_{eff}, Molar Refractivity *R*, and Ratio of Polarizability α versus Diamagnetic Susceptibility *X*, Crystallographic Radii R_c, the Radii of the Water Molecule in the First Hydration Sphere R_{w1}, and the Number *H* of Water Molecules in the Second Hydration Sphere

	N	N_m/N	PF	$D_1 \times 10$ (C m^{-2})	q_{eff}	R (cm^3 mol^{-1})	α/X ($\times 10^{18}$)	R_c (Å)	R_{w1} (Å)	H (Å)
F^-	5.05	2.04	0.736	1.25	−1	2.21	0.054	1.320	1.338	0.00
Cl^-	6.02	2.43	0.736	1.03	−1	8.63	0.079	1.810	1.358	0.00
Br^-	6.37	2.50	0.736	0.96	−1	12.24	0.088	1.964	1.362	0.00
Li^+	5.00	1.29	0.779	1.38	1	0.08	0.036	0.675	1.381	0.00
Na^+	4.92	1.74	0.782	1.32	1	0.65	0.060	1.004	1.409	0.00
K^+	5.12	2.19	0.774	1.22	1	2.71	0.084	1.376	1.415	0.00
Rb^+	5.22	2.30	0.774	1.18	1	4.10	0.089	1.485	1.419	0.00
Cs^+	4.75	2.76	0.772	1.22	1	6.89	0.094	1.626	1.422	0.00
Mg^{2+}	6.00	1.16	0.801	2.66	2	−0.70	0.062	0.720	1.358	6.19
Ca^{2+}	6.10	1.45	0.799	2.50	2	1.59	0.084	1.005	1.383	5.25
Sr^{2+}	6.65	1.54	0.797	2.28	2	2.65	0.089	1.197	1.393	4.14
Ba^{2+}	7.25	1.61	0.794	2.09	2	5.17	0.094	1.389	1.400	3.22
La^{3+}	9.00	1.18	0.803	2.83	2.86	6.30	0.093	1.216	1.333	7.18
Ce^{3+}	9.00	1.17	0.803	2.86	2.88	6.11	0.094	1.196	1.333	7.38
Pr^{3+}	9.00	1.15	0.803	2.89	2.89	5.92	0.094	1.179	1.333	7.55
Nd^{3+}	9.00	1.14	0.803	2.89	2.89	5.74	0.094	1.163	1.333	7.58
Pm^{3+}	8.99	1.12	0.803	2.89	2.88	5.55	0.094	1.144	1.333	7.55
Sm^{3+}	8.94	1.12	0.804	2.91	2.91	5.37	0.094	1.133	1.334	7.70
Eu^{3+}	8.71	1.14	0.805	3.05	2.99	5.18	0.094	1.113	1.336	8.61
Gd^{3+}	8.27	1.16	0.805	3.17	2.96	4.99	0.095	1.069	1.341	9.44
Tb^{3+}	8.05	1.17	0.806	3.27	2.97	4.81	0.095	1.042	1.344	10.15
Dy^{3+}	8.01	1.16	0.805	3.26	2.94	4.62	0.095	1.027	1.344	10.08
Ho^{3+}	8.00	1.15	0.806	3.32	2.98	4.43	0.095	1.019	1.345	10.48
Er^{3+}	8.00	1.14	0.806	3.32	2.97	4.25	0.095	1.006	1.345	10.48
Tm^{3+}	8.00	1.13	0.806	3.32	2.97	4.06	0.095	0.992	1.345	10.49
Yb^{3+}	8.00	1.12	0.806	3.36	3	3.88	0.095	0.984	1.345	10.80
Lu^{3+}	8.00	1.12	0.806	3.37	3	3.69	0.095	0.977	1.345	10.85
Ce^{4+}	11.69	1.00	0.805	3.35	3.77	10.85	0.090	1.131	1.329	10.74

TABLE 3: Values of Parameters b_0, b_1, and b_2 of Eq 5

	b_0	b_1	b_2		b_0	b_1	b_2
M^+	1.2291	0.1130	−0.0230	M^{3+}	1.2517	0.1920	−0.0615
M^{2+}	1.3013	0.1534	−0.0495	M^{4+}	1.5021	−0.2349	0.0777

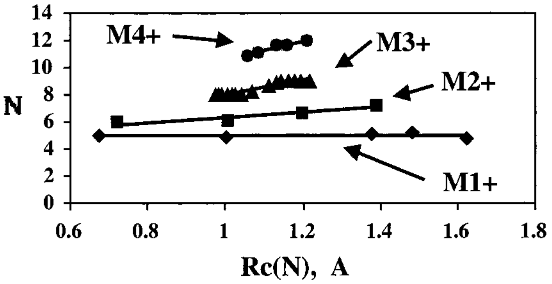

Figure 1. Variations of *N* versus $R_c(N)$, for halides, alkalis, alkaline earths, trivalent lanthanides, and tetravalent cerium and actinides.

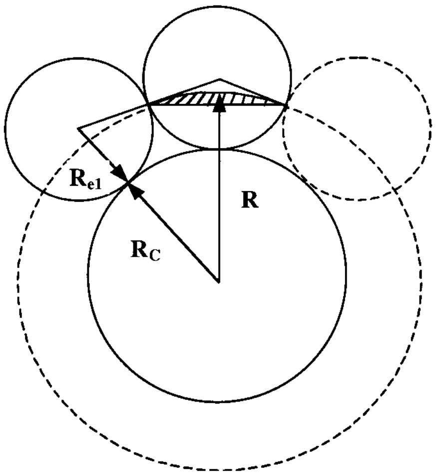

Figure 2. Scheme of water molecules coordinating to an ion in the first hydration sphere.

method is interesting for ionic species and has been introduced in the HYDRA program[1] but appears less accurate when covalent bonds occur.

Finally, the adopted *N* values are tabulated in Table 2. It is remarkable that the evaluated values obtained by the proposed model and eq 8 fit the data calculated by the HYDRA program within a 4% standard deviation and that, in all of the cases, the calculations are consistent with experimental determinations, taking into account the experimental accuracy.

Effective Charges. It is well-known that, at the beginning of both the lanthanide and actinide series, the ions form slightly covalent bonding. As the atomic number of an f ion increases, the degree of covalency decreases, reaching practically zero in the second part of the series. The effect is due to a degree of participation of the f electrons in bonding. The f orbitals are relatively diffuse in the beginning of lanthanide and actinide series. So, the f electrons of lighter lanthanides and actinides can be relatively delocalized to participate in the formation of binding molecular orbitals, thus forming a covalent bond. As the atomic number of an f ion increases, the f electrons become more and more localized, being screened from the outer influence by the closed 5p orbitals of lanthanides or 6p orbitals of actinides. This is known as lanthanide (actinide) contraction. So, for the heavier f ions, covalent bonding is replaced by an ionic one, leading, as one will see later in the paper, to a coincidence of ionic and experimental values of R_{w1}.

The effective charge (EC) of an ion is a useful characteristic, widely used both in classical and quantum chemistry. There are three main ways to obtain EC: Mulliken population analysis, the atomic polar tensor method, and topological analysis of the electron density population. A comparison of these methods is given in ref 12. There is also a special module of the Gaussian98 software[13] dedicated to the calculation of EC. Nevertheless, because of the very complicated electronic the structure of

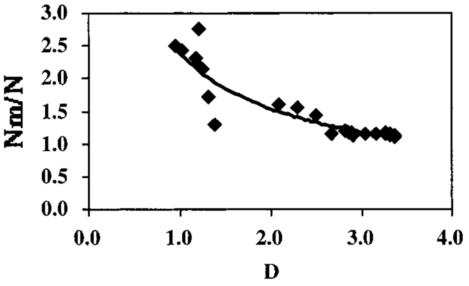

Figure 3. Variations of N_m/N versus the charge density $D = D_1 \times 10$ in C/m^2, for ions of charges from -1 to $+4$, and the obtained correlation.

lanthanides and actinides, there were, until now, no reliable methods for the calculation of EC for these ions. Thanks to the proposed model and EXAFS data on the structure of hydrated ions, we were able to calculate EC for hydrated lanthanide and actinide ions.

As mentioned in the previous paper,[1] the experimental values of the water molecule radii ($R_{w1,exp}$) in the vicinity of the trivalent lanthanide ions are smaller at the beginning of the series than the ionic values (R_{w1}) calculated by the electrostriction model.[1,2,11] A similar decrease (ΔR_{w1}) has also been observed at the beginning of the actinide series.[14] The difference, $\Delta R_{w1} = R_{w1} - R_{w1,exp}$, decreases with the atomic number for both series[1,14] and was assumed to be related to a covalent effect. To take this effect into account, the parameters of eq 1 were computed by excluding the first seven elements of the lanthanide series[1] where covalence could exist. Then, the ΔG(hyd) values of these elements were calculated[1] by assuming that the radius of the water molecule corresponds to its ionic value and that the charge of the cation is 3^+.

If we introduce now the experimental value $R_{w1,exp}$ in eq 1 instead of R_{w1}, six major terms will increase. The only possibility to evaluate correctly the free hydration energy, in agreement with the known experimental data, is to accept that the charge q of the species is decreased. It corresponds to a well-known fact that, for covalent species, the effective charge q_{eff} is less than the ionic charge q. Simultaneously, we also have to correct the absolute free hydration energy, (ΔG(hyd)) because it is derived from the conventional energy ($\Delta G(\text{hyd})_{conv}$) by the relation $\Delta G(\text{hyd}) = \Delta G(\text{hyd})_{conv} + q_{eff}\Delta G(\text{hyd})(\text{H}^+)$, where $\Delta G(\text{hyd})(\text{H}^+)$ is the absolute free hydration energy of the proton. That quantity, evaluated by numerous authors, is taken[13] equal to -1056 kJ mol^{-1}.

Thus, using eq 1, one is able to deduce consistent values of q_{eff} for all of the covalent species because the equation is a polynomial expression of q_{eff} of order 2. These data are reported in Table 2.

It is interesting to correlate q_{eff} with the experimental distance δ or, similarly, with the experimental radius of water. More precisely, we will compare the decrease of the radius ΔR_{w1} with the decrease of the charge Δq because both quantities are related to the covalent effect. We assume that the major part of the decrease of the distance is due to the ligand because the crystallographic radius is determined by considering compounds (oxides) which already contain a small covalent contribution. The variations of $\Delta q/q$ versus $\Delta R/R$ are reported in Figure 4. One observes, as expected, a simple (linear) correlation between the two quantities considered. The equation is

$$\Delta q/q = 1.858\Delta R_{w1}/R_{w1} \tag{9}$$

It signifies that the covalent effect could be quantified by the determination of the interatomic distances. Thus, a precise experimental determination of δ allows the evaluation of the effective charges.

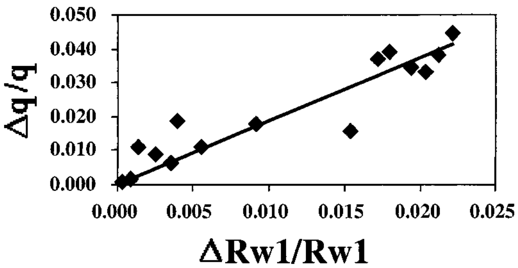

Figure 4. Variations of the $(3 - q_{eff})/3$ values versus $(R_{w1,ion} - R_{w1})/R_{w1}$, in the case of the trivalent lanthanide aquo ions.

TABLE 4: Values of Parameters of Eq 1

	a	b	c	d	e	f	g	δE^1
au	−423.93	−432.38	445.60	−324.38	−40.33	2.68	−99.99	−0.51

Finally, the introduction of the experimental values of δ and q_{eff} in the HYDRA[1] program permits the reevaluation of the eight parameters in relation 1. They do not differ significantly from those obtained previously, when pure ionic species were considered.[1] The new parameters are reported in Table 4.

It is interesting to verify that the obtained constants are in good agreement with the data that could be expected from the expressions which are functions of the fundamental constants.[1] All of the signs of the eight terms are consistent; moreover, the parameter a allows for an evaluation of the dielectric constant in the vicinity of the central ion, $\epsilon = 2.56$, which is consistent with a value of around 2 deduced from the electrostriction theory.[11] It is also interesting to observe that these data are not in agreement with the hypothesis made in the molecular dynamic calculations, where $\epsilon = 1$ is accepted. A small contribution, such as δE^1, is in good agreement with the experimental data.[16] Therefore, we are concluding that the proposed model has a physical meaning and that eq 1 does not have to be considered as an empirical expression.

To apply the procedure of hydration energy evaluation to a new species, we have to define the polarizability (α) and the susceptibility (X) (or α/X) which occur in the dispersion energy term.[1]

Because α is proportional to the molar refractivity[17] (R where $\alpha = 3.96 \times 10^{-19}R$ cm^3 mol^{-1}), we have reported R values tabulated from ref 17 in Table 2.

R has been tabulated[17] for many ions. The small weight[1] of the dispersion term, around 1%, permits the acceptance of a rough correlation between R and α/X with the atomic number Z or the charge of the ion. As in the previous paper,[1] the evaluations are based on α/X data corresponding to the rare gases Ne, Ar, Kr, and Xe and on the R values of ref 17.

For instance, the obtained expressions for trivalent lanthanides are

$$R = -0.186Z + 0.077$$

and

$$\alpha/X = -2 \times 10^{-6}Z^2 + 4 \times 10^{-3}Z + 16.9 \tag{10}$$

The data for the elements considered are reported in Table 2.

The number of water molecules H, which are situated in the second hydration shell, have been recalculated, taking into account the existence of the effective charge. The program HYDRA[1] has been modified for this purpose, and new data are

TABLE 5: Calculated Values of Parameters

	$d\delta/dT$	dN/dT	$d\epsilon/dT$	$d\mu/dT$	dp_w/dT	de/dT
value	5.69×10^{-4}	2.38×10^{-3}	-2.33×10^{-3}	-5.02×10^{-4}	-4.71×10^{-4}	-4.99×10^{-4}
units	Å T^{-1}	T^{-1}	T^{-1}	C Å T^{-1}	C Å^2 T^{-1}	T^{-1}

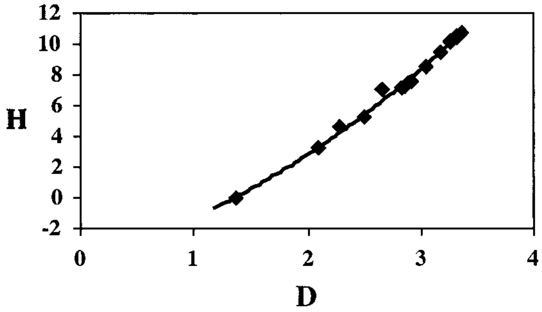

Figure 5. Variations of H with the charge density on the primary sphere D ($D = D_1 \times 10$ in C/m^2).

TABLE 6: Experimental and Calculated Entropies of the Aquo Ions $S°_{aq}$, Entropies of the Gaseous Ion $S°$(ion,gas), and Experimental and Calculated Hydration Entropies ΔS(hyd) in the Absolute Scale Assuming[15] $S°_{aq}(H^+) = -22.2$ eu

ion	$S°_{aq}$ exp, conv	$S°$(ion,gas) (eu)	ΔS(hyd) exp, abs	ΔS(hyd) calc, abs	$S°_{aq}$ calc, conv	$S°_{aq}$(exp) − $S°_{aq}$(calc)
F^-	−14	145	−137	−129	−6	−8
Cl^-	57	153	−74	−85	45	12
Br^-	82	163	−59	−74	67	15
Li^+	14	133	−141	−141	14	0
Na^+	60	148	−110	−102	68	−8
K^+	103	154	−74	−69	107	−4
Rb^+	124	164	−62	−60	126	−2
Cs^+	133	170	−59	−48	144	−11
Mg^{2+}	−138	149	−331	−339	−146	8
Ca^{2+}	−53	155	−252	−279	−80	27
Sr^{2+}	−33	165	−242	−244	−35	2
Ba^{2+}	10	170	−205	−215	−1	11
La^{3+}	−209	170	−446	−437	−203	−6
Ce^{3+}	−205	185	−457	−445	−196	−9
Pr^{3+}	−207	189	−462	−451	−198	−9
Nd^{3+}	−206	190	−463	−454	−200	−6
Pm^{3+}	−200	189	−456	−455	−202	2
Sm^{3+}	−207	186	−460	−458	−207	0
Eu^{3+}	−216	181	−463	−472	−225	9
Gd^{3+}	−219	189	−475	−476	−221	2
Tb^{3+}	−224	193	−484	−484	−225	1
Dy^{3+}	−229	195	−491	−482	−221	−8
Ho^{3+}	−229	196	−492	−491	−229	0
Er^{3+}	−235	196	−497	−492	−230	−5
Tm^{3+}	−236	194	−497	−493	−234	−2
Yb^{3+}	−241	190	−498	−501	−244	3
Lu^{3+}	−264	173	−504	−503	−263	−1
Ce^{4+}	−419	170	−678	−671	−417	−2

reported in Table 2. As indicated in the previous paper, we can observe a simple relation between H and D (Figure 5), and a polynomial relation is deduced:

$$H = 0.6896D^2 + 2.076D - 4.076 \tag{11}$$

Entropy Model for Monatomic Aquo Ions. Different models of the entropy of hydration have been discussed recently in a general review by Bockris and Reddy.[18] It contains an evaluation of several components of the hydration entropy, such as the translational entropy, parts due to solvationally coordinated water molecules, and the structure breaking region. Calculations include relatively complex evaluations of librational and vibrational contributions. The comparison of the calculated data versus the experimental data shows a significant disagreement. For monovalent ions only, the obtained standard deviation is 40 eu. Therefore, we undertake entropy modelization, similar to that which we have chosen for the ion−solvent interaction model.

Because the hydration entropy (ΔS(hyd)) is expressed by the derivation of the free hydration energy versus temperature, the proposed entropy model is based on the derivation of eq 1 versus temperature T. This procedure is justified because eq 1 has essentially a physical and not an empirical significance.[1] We have considered the derivative versus temperature of six quantities which are present in the equations of the parameters[1] of eq 1: $d\delta/dT$, dN/dT, $d\epsilon/dT$, $d\mu/dT$, dp_w/dT, and de/dT.

$$\Delta S(\text{hyd}) = \mathbf{M}_1\, d\delta/dT + \mathbf{M}_2\, dN/dT + \mathbf{M}_3\, d\epsilon/dT + \mathbf{M}_4\, d\mu/dT + \mathbf{M}_5\, dp_w/dT + \mathbf{M}_6\, de/dT \tag{12}$$

The matrices $\mathbf{M}_1$−$\mathbf{M}_6$ have the following expressions, after neglecting terms having small weights:

$$\mathbf{M}_1 = -A_1q^2/(\delta + R_{w1})^2 - 2B_1F|q|N/\delta^3 - 3C_1F^2qN/\delta^4 - 4D_1FNq^2/\delta^5 + 3F_1\delta^2$$

$$\mathbf{M}_2 = B_1F|q|/\delta^2 + C_1F^2q/\delta^3 + D_1Fq^2/\delta^4$$

$$\mathbf{M}_3 = Aq^2/(\delta + R_w)\epsilon^2 - FB_1|q|N)/\epsilon\delta^2 - F^2C_1qN/\epsilon\delta^3 - FD_1q^2N/\epsilon\delta^4$$

$$\mathbf{M}_4 = FB_1|q|N/\delta^2$$

$$\mathbf{M}_5 = F^2C_1qN/\delta^3$$

$$\mathbf{M}_6 = 1000H$$

The constants A_1, B_1, C_1, D_1, and F_1 correspond to the parameters a, b, c, d, and f of eq 1 after multiplication by 1000 for a kJ → J unit transformation. The constant A in the expression for $\mathbf{M}_3$ is

$$A = -N_A e_0^{\,2}/8\pi\epsilon_0$$

where N_A is Avogadro's number, e_0 is the elementary charge, and ϵ_0 is the dielectric constant.

Because the six derivatives in eq 10 are not measured or are not possible to evaluate, we have obtained these characteristics by using the experimental entropies of halide, alkali, alkaline-earth, and trivalent lanthanide ions. They are reported in Table 5. Using these parameters for all of the considered ions, we have calculated ΔS(hyd) and deduced the entropy of the aquo ion $S°_{aq}$ because

$$S°_{aq} = \Delta S(\text{hyd}) + S°(\text{ion,gas})$$

The entropy of the gaseous ion $S°$(ion,gas) is obtained by the Sackur−Tetrod equation. We have compared the obtained data with the published ones[19] in Table 6. In the last column, $S°_{aq}$(exp) − $S°_{aq}$(calc) allows for the conclusion that the standard deviation between the experimental and the calculated data is as small as 9 eu, taking into account a series of ions with charges from −1 to +4. That uncertainty is less than the given error in the experimental data. Therefore, we can conclude that the proposed entropy model is rather reliable. Because it is based on characteristics which have physical meaning, it allows for the prediction of the entropies of various monatomic ions.

Conclusions

We have shown that the proposed models of hydration and entropy could be applied for a large number of ionic and covalent monatomic species. These models have been tested successfully for a number of ions with charges from -1 to $+4$, including all of the trivalent lanthanides and the tetravalent cerium ion. Free hydration energies and entropies have been evaluated which are in excellent agreement with available experimental data. Important characteristics of the aquo ion have been determined or predicted, such as the coordination number, the number of water molecules in the second hydration sphere, and the effective charge. The obtained parameters of the models have physical meaning and can be compared with the experimental data to control the validity of the calculations.

Besides the two fundamental equations (1 and 10), six empirical relations have been established which point out the decisive characteristics of the coordination number N, the effective charge q_{eff}, the charge density D, the crystallographic radii R_c, and the radius R_{w1} of water molecules. These relations are useful to calculate and predict the important properties of an ion when the HYDRA program is not used.

(1) For each ion having the well-known values of the crystallographic radii for different coordination numbers,[3,4] we have obtained sets (Table 1) of polynomial relations for $R_c = f(N)$.

(2) From the correlation between the ratio of the maximum possible coordination number N_m value over the effective N value versus the charge density D (Figure 3 and eq 8), it is possible to predict, or define, N values when no reliable measurements are available. The program HYDRA can also derive coordination numbers by the adjustment of the calculated and experimental free hydration energy or by the comparison of the experimental and calculated distances between the ion and oxygen atom of the primary hydration sphere.

(3) For each series of ions, the radius of the water molecule is not a constant and, considering an ionic system, is a function of R_c: $R_{w1} = f(R_c)$ (see eq 5).

(4) A packing factor PF is defined for a given ion depending on the charge density D (see eq 4).

(5) When the charge density D_1 is higher than a certain minimum value ($D_1 = 0.135$ in SI units), the number H of water molecules in a second hydration sphere is related to D_1 (Figure 5 and eq 11). Thus, H can be evaluated for any monatomic species.

(6) When covalent species are considered, the value of R_{w1} obtained from the experimental ion−water distance is proved to be regularly smaller than the corresponding calculated ionic value. We used experimental distances instead of ionic ones to calculate the ΔG(hyd) of aquo ions with covalent bonding. In the ionic model, ΔG^0(hyd) is expressed through the terms $\sim q^n/\delta^m$ ($n = 1$ and 2; $m = 1-6$), so, to save the value of $\Delta G°$(hyd) when δ (and hence R_{w1}) is diminished, one has to reduce an ionic value of q to a smaller effective one. Thus, using the experimental values of ΔG^0(hyd), we were able to obtain effective charges q_{eff} of lanthanide aquo ions (see Figure 4 and Table 2). A linear correlation is established between $\Delta R_{w1}/R_{w1}$ and $\Delta q/q$ (see eq 9).

(7) An entropy model is deduced by the derivation of the ion−solvent interaction model (eq 12). It depends on six parameters, which allow an accurate evaluation of the entropy for ionic or covalent monatomic ions.

Finally, considering the basic characteristics of an aquo ion and the obtained equations which relate these characteristics with each other, it appears that the fundamental properties of a monatomic ion with a given oxidation state could be derived by the knowledge of two main characteristics: the crystallographic radius and the cation−oxygen distance. These data can be determined accurately by X-ray diffraction and X-ray absorption spectroscopy methods. The proposed models allow the evaluation of not only ΔG(hyd), entropies, and the effective charge of the aquo ions but also of other properties of ions in solution, such as the redox potentials, the size of the aquo ion, and the related characteristics such as transport properties. They could also be used to refine models of the activity coefficients considering more realistic characteristics of the ion.

Such models of the aquo ion properties will be used to predict and quantify thermodynamic properties of actinide aquo ions because many experimental data are missing. Also, we project to extend our models to d elements and, in this case, to consider the ligand field effect.

References and Notes

(1) David, F.; Vokhmin, V.; Ionova, G. *J. Mol. Liq.* **2001**, *90*, 45.
(2) David, F.; Fourest, B. *New J. Chem.* **1997**, *21*, 167.
(3) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.
(4) David, F. *J. Less-Common Met.* **1986**, *121*, 27.
(5) Sham, T. K. *Phys. Rev. B*: *Condens. Matter* **1989**, *40* (9), 6045.
(6) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157.
(7) Marcus, Y. *Chem. Rev.* **1988**, *88*, 1475.
(8) Moll, H.; Denecke, M. A.; Jalilehvand, F.; Sandström, M.; Grenthe, I. *Inorg. Chem.* **1999**, *38*, 1795.
(9) Allen, P. G.; Bucher, J. J.; Shuh, D. K.; Edelstein, N. M.; Reich, T. *Inorg. Chem.* **1997**, *36*, 4676.
(10) Conradson, S. D.; Clark, D. L.; Neu, M. P.; Runde, W.; Tait, C. D. *Los Alamos Sci.* **2000**, *26*, 364.
(11) Conway, B. E. Ionic Hydration in Chemistry and Biophysics. *Studies in Physical and Theoretical Chemistry*; Elsevier: New York, 1981; p 545.
(12) Giolowski, J.; Kay, P. J.; Ritchie, J. P. *J. Phys. Chem.* **1990**, *94*, 148.
(13) *Gaussian98*; Gaussian Inc.: Pittsburgh, PA, 1998.
(14) David, F.; Revel, R.; Fourest, B.; Hubert, S.; Le Du, J. F.; Den Auwer, C.; Madic, C.; Morss, L. R.; Mikhalko, V.; Vokhmin, V.; Ionova, G.; Berthet, J. P.; Ephritikhine, M. Proceedings of the Actinide XAS 98 Conference, Grenoble, Oct 2−4, 1998; AEN Report 1999.
(15) Marcus, Y. *Ion Solvation*; John Wiley and Sons: New York, 1985.
(16) Jørgensen, C. K. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3127.
(17) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997; p 139.
(18) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*, 2nd ed.; Plenum: New York, 1998; Vol. 1.
(19) Bard, A.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solution*; IUPAC Marcel Dekker: New York, 1985.