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Hydration Energies of the Divalent Lanthanides and Alkaline Earth Elements

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Abstract

The hydration energies of the divalent lanthanide ions and those of alkaline earth elements are proved to be dependent on their ionic radii. This dependence is described by one and the same equation.

By now all the lanthanides from lanthanum to lutetium have been obtained in their divalent states, and the values of their standard oxidation potentials $E^\circ_{Ln^{3+}/Ln^{2+}}$ have been determined [1]. Besides, we showed in ref. 2 that $E^\circ_{Ln^{3+}/Ln^{2+}}$ is a linear function of the f–d excitation energy (E_{fd}) for all the lanthanides having an $f^n d^0$ electron configuration. The equations

$$E^\circ_{Ln^{3+}/Ln^{2+}} = (0.80 \pm 0.03)E_{fd} - (4.12 \pm 0.08) \qquad (\text{Pr–Eu})^* \qquad (1)$$

and

$$E^\circ_{Ln^{3+}/Ln^{2+}} = (0.84 \pm 0.09)E_{fd} - (4.64 \pm 0.27) \qquad (\text{Dy–Yb})^* \qquad (2)$$

hold for praseodymium to europium and dysprosium to ytterbium, respectively.

Comparing both these equations with the well-known equation of the dependence of the standard oxidation potential $E^\circ_{M^{3+}/M^{2+}}$ on the ionization potential and hydration energy:

$$E^\circ_{M^{3+}/M^{2+}} + 4.43 = \Delta G^\circ_{ion} + \Delta G^\circ_{hydr}(M^{3+}) - \Delta G^\circ_{hydr}(M^{2+}) \qquad (3)$$

where 4.43 V is the standard thermodynamic electrode potential of the hydrogen electrode [3], ΔG°_{ion} is the ionization energy calculated from the value of the third ionization potential I_3 [4], and $\Delta G^\circ_{hydr}(M^{2+})$ and $\Delta G^\circ_{hydr}(M^{3+})$ are the hydration energies of the di- and trivalent ions [2], we can see that eqns. (1), (2) and (3) are of the same type.

Representing the ionization energy from the ground state level as a sum of the f–d excitation energy (E_{fd}) and ionization energy from the energetically higher d-level (ΔG°_{Id}), eqn. (3) can be rewritten:

$$E^\circ_{M^{3+}/M^{2+}} = E_{fd} + \Delta G^\circ_{Id} + \Delta G^\circ_{hydr}(M^{3+}) - \Delta G^\circ_{hydr}(M^{2+}) - 4.43 \qquad (4)$$

In this equation, the prefactor to E_{fd} equals 1, while in eqns. (1) and (2) it equals 0.80 and 0.84, respectively. This difference may be accounted for by the fact that either the sum of $\Delta G^\circ_{Id} + \Delta G^\circ_{hydr}(M^{3+}) = \Delta G^\circ_{hydr}(M^{2+})$, or some of its components depend on the f–d excitation energy. Therefore, the first problem was to find out whether the hydration energy of the divalent lanthanides is dependent on the f–d excitation energy. We used the hydration energy values obtained in ref. 2 and the f–d excitation energy data from ref. 4. Figure 1 shows the dependence of the hydration energy of the divalent lanthanides on the f–d excitation energy of their free ions. As seen from Fig. 1, the hydration energy is generally dependent on the f–d excitation energy. So the problem was to determine whether such a correlation had a physical meaning or was merely coincidental. To do so, we needed to compare the hydration energies of the divalent lanthanides with those of the alkaline earth ions, since the latter are spherically symmetric and, therefore, do not exhibit

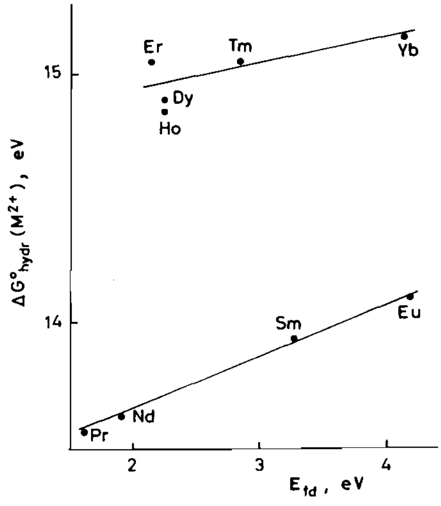

Fig. 1. Dependence of the hydration energy of divalent lanthanides on the f–d excitation energy.

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*In this and the following equations energy values are given in eV for simplicity reasons. Coefficients before any energy value are given in e^{-1}.

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a ligand-field stabilization effect. We used the values of hydration enthalpies from ref. 5 and hydration entropies from ref. 6 to calculate the hydration energies for the alkaline earth ions. Based on a modified Born equation [6] it was important to consider whether $[\Delta G^{\circ}_{\mathrm{hydr}}(\mathrm{M}^{3+})]^{-1}$ was linearly dependent on the ionic radius R. As is seen from Fig. 2, the values of $[\Delta G^{\circ}_{\mathrm{hydr}}(\mathrm{Ln}^{2+})]^{-1}$ follow the line connecting the points corresponding to the Ca, Sr and Ba hydration energies. Thus, the divalent lanthanides prove to be close analogues to the alkaline earth elements. Consequently, the dependence of the Ln^{2+} hydration energy on the f–d excitation energy shown in Fig. 1 is only by chance. Therefore, this work establishes the fact that the hydration energies of alkaline earth elements and those of the divalent lanthanides are described by one and the same equation:

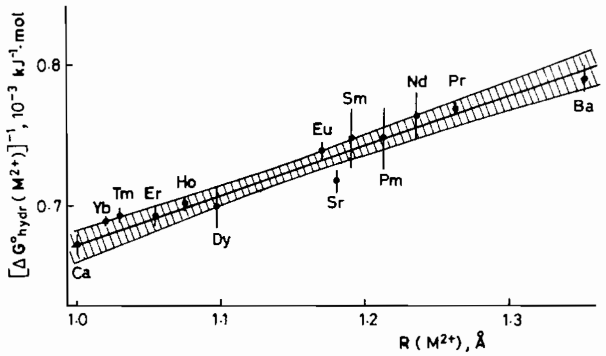

Fig. 2. Dependence of $[\Delta G^{\circ}_{\mathrm{hydr}}(\mathrm{M}^{2+})]^{-1}$ on the ionic radius.

$$[\Delta G^{\circ}_{\mathrm{hydr}}(\mathrm{M}^{2+})]^{-1} = \mathrm{f}(R),$$

where R is the ionic radius of an element.

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