

Hydration Structure of Trivalent Lanthanides and Actinides

What can we learn from hydration structure of felements?

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SPring.8



Hydration Structure and Hydration Number

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Lanthanide and Actinide Contraction

Simple interpretation of lanthanide contraction

16% decreases in ionic radius from beginning to end.

Lanthanide contraction



La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu





Paola D'Angelo et al., IC (2013)

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Insufficient explanation for the previous results

- The reported hydration bond distances ranged.
- The relation between Tetrad effect and bond properties.
- Importance of Hydration Number



Extraction behavior of Lanthanide by DPDO



On the intra-series separation of lanthanides or actinides

The ionic radius as an index of the coordination space and the effective nuclear charge of f-element are the most basic parameters for consideration of intra-series separation of f-element.







Purpose of this study

- Hydration bond distances of actinides and lanthanides will be determined by EXAFS methods. Regarding actinides, we try to get the first data as the ionic radius of Es³⁺.
- 2. The obtained hydration bond distances of the felements will be discussed from the viewpoints of the actinide and lanthanide contraction and hydration number.
- 3. We will discuss hydration behavior from the viewpoints of shielding effect.



Measurement System

Experimental Setup at BL22XU, SPring-8







EXAFS for trace amount of materials



May 20-23rd, 43th ASC



Hydration structures of Ln(III)

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"Einsteinium Brake" of Actinide Contraction Japan Atomic Energy Agency On Hydration



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Radial Distribution Function Theoretical Calculation for Ionic Radius



Solving a fully-relativistic Dirac equation with an exchangecorrelation potential in a local-density approximation

Condition: 5fⁿ & 5fⁿ⁻¹6d¹ configuration

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Consideration of Shielding by 1/<r>

For hydrogen atom wave functions, it is not the average ionic radius that varies linearly with effective nuclear charge but rather the average inverse ionic radius. This suggests that the inverse of the lanthanide ionic radius (where x is the number of f electrons in the lanthanide ion of interest, treated as a continuous variable), can be represented by a linear equation:

$$\frac{1}{r(x)} = a + bx \qquad a = \frac{1}{r_0} \qquad b = \frac{\partial (1/r(x))}{\partial x}$$

As will be shown, this is mathematically equivalent to the Slater shielding formula.

Raymond et al., 2010



1/<r> analysis

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It could be more reasonable that the correlation with the hydration ionic radius is determined by the shielding efficiency of f-orbital electrons and the stabilization of hydration rather than the change in coordination number.



Comparison with Hydration structure based on crystallography



This work: Slope: about 0.014 for both the Ln and An

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It is reasonable to assume that structural averaging has occurred in solution. •15



Summary and Conclusion

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- We determined hydration structure of lanthanide and actinides.
- We observed "Einsteinium Break" (ESB) of actinide contraction on hydration behavior.
- Breaking phenomena could be caused by electronic configuration change of these ions from the total consideration of actinide and lanthanide results
- The hydration ionic radius is possibly determined by the relation between the shielding efficiency of f-electron and structural stabilization in solution.



END of Talk

Thank for your kind attention