VALENCE AND IONIC SIZE OF AQUEOUS ACTINIDE IONS

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VALENCE AND IONIC SIZE OF AQUEOUS ACTINIDE IONS*

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ABSTRACT

A comparison of crystallographic radii of actinide ions with their stability in aqueous solutions shows that except for Ac$^{3+}$ and Th$^{4+}$, the simple actinide ions stable in aqueous solutions have ionic radii between 0.93 and 1.05 Å. Extrapolation of crystal radii to the heavy actinides suggests that 2+ ions of Fm, Es, and possibly Cf could exist in aqueous solutions, and that 4+ ions of elements heavier than Cf would be unstable.

INTRODUCTION

The actinide ions range in valence from 2+ to 7+, with the higher valences being more stable for the lighter elements of the series, and lower valences more stable at the heavy end of the series. This unusual range of valences, especially when compared with the lanthanide elements, has been frequently discussed in

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terms of electronic structure. This paper will discuss the influence of ionic size in determining the valence stability of actinide ions in aqueous solution.

DISCUSSION

As the valence of an actinide ion increases, the ion becomes smaller; typical ionic radii are about 1 Å for 3+ ions, 0.9 Å for 4+ ions, 0.88 Å for 5+ ions, and 0.82 Å for 6+ ions. The charged ions attract ligands into their coordination spheres in condensed systems, such as aqueous solutions or solid compounds. An actinide ion, in most systems, has little covalency, and so may be described as a positively charged particle surrounded by ligands that shield the ion from its environment. The ability of the actinide ion to bind ligands will depend both on its size and charge; the number of ligands in its coordination sphere will be limited by the repulsion of the ligands toward each other. The electrostatic balance of ligands and ions will be unstable for large ions of low charge and for small ions of high charge. Actinide ions with higher valences (5+, 6+, and 7+) are stabilized by forming covalent oxygenyl ions, such as uranyl (UO$_2$$^{2+}$) or neptunyl (NpO$_2$$^+$). This is possible because of participation of the 5f electrons in the covalent bonds. These highly charged actinide ions form larger ions with reduced valence by strong covalent bonding with two oxygen ions; as a unit, the product ions coordinate weakly with liquids and have relatively large hydrolysis constants.
The hydrated 3+ and 4+ ions cannot be stabilized in this fashion because their 5f orbitals are not accessible to overlap by ligand orbitals. These aquo ions should show the influence of size on valence stability, although for some ions favorable electronic configurations will be important and may alter conclusions based on size considerations alone.

The ionic radii of 3+ actinides with coordination number 6 (CN6) and of 4+ actinides (CN8) are shown in Figure 1 from the compilation of Shannon and Prewitt.¹ These ionic radii were derived empirically from oxide structures and additively reproduce interatomic distances in oxide crystals for the proper CN. They are used to make relative comparisons of charge and size even though they may not represent the actual sizes of the ions in solution. Neither trivalent lanthanides nor trivalent actinide ions are normally CN6 in solution, but usually CN8 or CN9. Quadrivalent actinides are normally CN8 in solid compounds, although there are exceptions, and are probably CN8 or CN9 in solution. The relative ionic sizes of 3+ actinides and 4+ actinides as shown are probably reasonable, but whether these values represent ionic radii in aqueous solutions is unknown.

Using Figure 1 as a basis for comparing ionic sizes, all the actinide ions stable toward water were found to have ionic radii between 0.925 and 1.05 Å except Ac³⁺ and Th⁴⁺. U³⁺ reduces water, and is not considered a stable ion.
Stabilities of several ions with aquo-stable valences are strongly influenced by electronic configuration. Ac\(^{3+}\), Th\(^{4+}\), and Pa\(^{5+}\) have 5f\(^0\) shells, a particularly stable configuration. Ions with the 5f\(^7\) sub-shell, Cm\(^{3+}\) and Bk\(^{8+}\), are also configuration-stabilized. The No\(^{2+}\) ion is certainly stabilized by its closed 5f\(^{14}\) shell. However, the stability or instability of other valences is consistent with the influence of ionic size. Md\(^{2+}\) has both a favorable electronic configuration and a favorable ionic radius; Th\(^{3+}\) has neither. The electronic configuration of Pa\(^{3+}\) (5f\(^2\)) is not unfavorable, but its ionic radius is too large for stability.

The ionic radii of 3+ actinides are extrapolated in the figure from the known ionic radii of Bk\(^{3+}\), Cf\(^{3+}\), and Es\(^{3+}\) on to Lr\(^{3+}\). To estimate the relative size of 2+ actinide ions, the difference in radii between 3+ and 4+ aquo actinide ions (0.06 Å) of the same element was assumed to be about the same as between 2+ and 3+ actinide ions. Since No\(^{2+}\) and Md\(^{2+}\) can be prepared in solution, their 2+ ions are shown as having ionic radii 0.06 Å greater than the extrapolated radii for 3+ ions. The ionic radius curve for 2+ actinides is an extrapolation of a line connecting these two points.

The extrapolated ionic radii for 2+ actinide ions suggest that Fm\(^{2+}\), Es\(^{2+}\), and possibly Cf\(^{2+}\) would be stable in aqueous solution. Despite its favorable electronic configuration, Am\(^{2+}\) is too large to be stable. The extrapolation of the radii of 4+
actinide ions suggests also that 4+ ions are unlikely to be stable in aqueous solutions of Cf and heavier 5f elements because of an unfavorable ionic size. Nugent and coworkers\textsuperscript{2,3} have estimated the oxidation potentials for 2+ – 3+, and 3+ – 4+ couples for the actinide ions by a semi-empirical method based on data from charge-transfer spectra. The predictions of valence-state stability made by this method are essentially the same as those presented here.

These qualitative considerations of ionic size are consistent with the known stability of aqueous actinide ions and provide an explanation for the stability of some valences that is, in general, more useful than predictions based solely on electronic configuration. The actinide ions are coordinated electrostatically with water and their stability toward oxidation and reduction in solution depends primarily upon a balance of electrostatic forces.
REFERENCES


FIGURE 1. Ionic Radii of Actinide Ions