

Environmental Management Science Program

Project ID Number 54595

f-Element Ion Chelation in Highly Basic Media

Robert T. Paine
University of New Mexico
Albuquerque, New Mexico 87131
Phone: 505-277-1661
E-mail: rtpaine@unm.edu

June 1, 1998

f-Element Ion Chelation in Highly Basic Media

Robert T. Paine, University of New Mexico

Research Objective

A large percentage of high-level radioactive waste (HLW) produced in the DOE complex over the last thirty years temporarily resides in storage tanks maintained at highly basic pH. The final permanent waste remediation plan will probably require that liquid and solid fractions be chemically treated in order to partition and concentrate the dominant hazardous emitters from the bulk of the waste. This is no small task. Indeed, there does not exist a well developed molecular chemistry knowledge base to guide the development of suitable separations for actinide and fission products present in the strongly basic media.

The goal of this project is to undertake fundamental studies of the coordination chemistry of f-element ions and their species formed in basic aqueous solutions containing common waste treatment ions (e.g., NO_3^- , CO_3^{2-} , organic carboxylates, and EDTA), as well as new waste scrubbing chelators produced in this study. The experimental agenda includes:

1. Studies of the speciation of Sr and Ln ions in basic solutions with and without common counterions;
2. Preparations of new multifunctional ligands that may act as strong, ion-specific chelators for Sr and/or Ln ions in basic media; and
3. Studies of the coordination and dissolution behavior of oxide-hydroxide species, as well as insoluble sols, gels, and precipitates in combination with new chelating ligands.

It is anticipated that this coordination chemistry will facilitate the design of advanced separation schemes required for handling the complex waste matrices found at the Hanford HLW facility.

Research Progress and Implications

As of 5/1/98 (19 months of 36-month project) the following advances have been realized.

1. Hydrolysis Chemistry

The pH dependence of the hydrolysis of nitrate salts of Sr(II), Y(III), La(III), Nd(III), and Er(III) have been reexamined by use of pH titrations and nephelometry. Particular attention was given to determining the pH for the onset of hydrolysis as well as the kinetics of particle growth at onset. The pH values for hydrolysis onset generally agree with related data in the literature. Following these measurements we have examined the pH shifts in hydrolysis onset as a function of counterion. We have chosen to study several ions typically present in waste media (e.g., NO_3^- , Cl^- , acetate, oxalate), as well as known chelating anions. A selected collection of these data will be presented in the poster paper. As expected, many of these ions cause significant shifts in the pH for hydrolysis onset due to competing association equilibria. Following these studies we have examined hydrolysis onset shifts caused by new phosphonic acid chelators prepared in our group. Dramatic shifts are encountered in some cases comparable to those observed with EDTA. For example, for La(III) the pH shifts are typically 6 pH units.

In related work, we have also studied the dissolution properties of lanthanide oxide-hydroxide precipitates by complexing anions. In this regard we have observed that several of our new phosphonic acids are very active at precipitate dissolution. In support of this work, we have recently begun to structurally analyze the precipitates and the dissolution complexes by use of solution and solid-state NMR as well as by X-ray light scattering.

2. New Complexant Development

Our initial efforts have shown that several phosphonic acids chelate with Ln(III) ions in basic media. In particular, we have found that 1 and 2 are particularly effective. This has led to an ambitious effort to prepare a second group of chelators listed as 3-5, which we expect to have improved extraction characteristics.

Planned Activities

During the remaining 15 months of the project we expect to continue our study of the interactions of phosphonic acid based ligands with soluble molecular, and oligomeric sol and gel species formed by Ln(III) ions in basic aqueous solutions. We will further characterize the features that are responsible for solubilizing the Ln oxide-hydroxide species and we will employ spectroscopic techniques to determine the nature of the structures formed in soluble complexes. The results will be crucially important to the characterization of soluble species present in tank waste and they will aid in the design of complexants that should be useful for partitioning these and related actinide species in basic media.

Other Access To Information

Two publications are in preparation describing initial results and specific data are available from the PI at UNM.

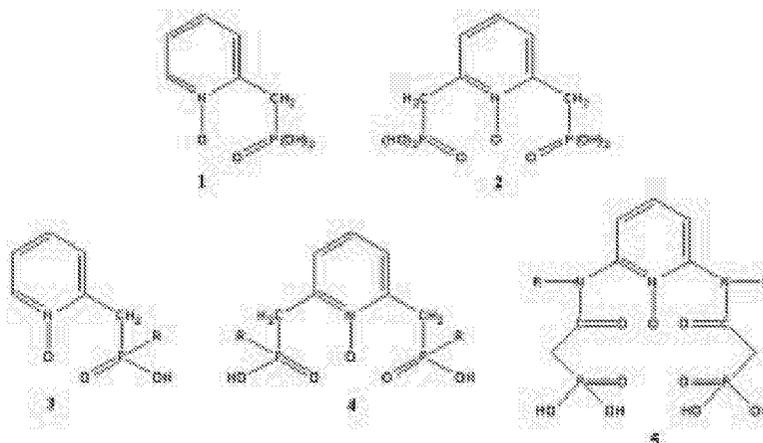


Figure 1