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DIPHOSPHONIC ACID COMPLEXANTS FOR IMPROVED SEPARATION EFFICIENCY OF TRANSURANIC ELEMENTS

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Thermodynamic parameters describing the complexation of tri-, tetra-, and hexavalent lanthanide/actinide metal ions by six diphosphonic acid ligands with different geometric arrangements of the diphosphonic acid groups and the carbon backbone have been measured. The results indicate that the strongest complexes are formed with ligands having two phosphonate binding groups attached to the same carbon atom of the organic backbone (1,1-diphosphonates), and that the water-soluble complexes are formed with protonated ligand species. The ligands are acidic but not corrosive. Their actinide complexes are more soluble and stable than the carboxylate or aminopolycarboxylate complexes that are currently used in actinide processing as aqueous stripping agents. Using the stability constants determined in this work, calculations indicate that more efficient separation/recovery processes could be designed to take advantage of the unique properties of these ligands. For example, diphosphonate complexants could be used to more effectively remove residual radioactivity from solvent extraction process streams (e.g., PUREX or TRUEX for treatment and isolation of transuranic elements). Improving the level of decontamination of recycled extractant reagents reduces the potential for worker exposure, extends the useful lifetime of the extractant solution or ion exchange resin, and decreases the volume of wastes that must be placed in a deep geologic repository. Research on these reagents, supported by the Division of Chemical Sciences, is being conducted by Ken Nash, Paul Rickert, Evan Appelman, and Lester Morss of the Heavy Elements Coordination Chemistry Group in the Chemistry Division at Argonne National Laboratory. Several papers describing this research are in print.

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In the processing of radioactive wastes, five classes of aqueous complexants typically are used for different purposes: inorganic acids (nitric, hydrofluoric), monocarboxylic acids (lactic, α -hydroxyisobutyric), polycarboxylic acids (oxalic, citric), aminopolycarboxylic acids (EDTA, DTPA), and diphosphonic acids (1-hydroxyethane-1,1-diphosphonic, vinylidene-1,1-diphosphonic). The use of each of these reagent classes carries certain advantages and liabilities. Inorganic anions are very soluble but they form weak complexes and are moderately corrosive. Mono- and polycarboxylic acids form stronger complexes, but only at reduced acidity, and their metal complexes are often of limited solubility. Aminopolycarboxylic acids form very strong complexes at $\text{pH} > 2$, but are resistant to environmental/biological degradation and hence represent a long-term environmental hazard. In particular, aminopolycarboxylates have been associated with the generation of H_2 gas in radioactive-waste storage tanks, and with the migration of radionuclides from low-level waste disposal sites. Diphosphonic acids form the strongest, moderately soluble complexes, are acidic but not corrosive to metal surfaces, and can be prepared with molecular geometries that are readily susceptible to thermal/oxidative degradation. The principal disadvantage of diphosphonic acid complexants is that they decompose to produce phosphate, which is not compatible with present formulations for high-level radioactive-waste glasses.

The Heavy Elements Coordination Chemistry Group, under the direction of Ken Nash and supported by the Division of Chemical Sciences, has recently completed a study of the thermodynamics of protonation and complexation of europium(III), thorium(IV), and uranium(VI) by a series of simple diphosphonic acid chelating agents to assess their potential for application in actinide-waste

processing. By examining the basic thermodynamics of the complexation of these three metal ions, guiding principles for the design of new ligands are obtained. The thermodynamic data also permit the calculation of relative efficiency of complexants for separations applications.

The basic structure of the diphosphonic acid complexants forming the strongest complexes is:

The substituents X and Y are adjusted to alter the solubility of the metal complexes, acidity of the ligands, and their tendency toward spontaneous decomposition. Six different complexants have been thoroughly investigated with another six presently undergoing evaluation. Carboxylate substitution and ring expansion lead to weaker complexes, which may ultimately permit the design of more selective ligands. Certain substituents introduced into the β position (i.e., one carbon atom removed from the 1,1-diphosphonate group) induces increased instability in the complexant and so enhances the decomposability of the reagent.

The relationship between metal complex stability and ligand protonation constants has long been recognized as a reliable indicator of relative complex strength. The data in Figure 1 demonstrate the enhanced complexing ability of the diphosphonic acid ligands over carboxylic and aminopolycarboxylic acid complexants. In this figure, the stability constants for the diphosphonic acids (solid symbols), as determined by Ken Nash, are 2 to 5 orders of magnitude greater than those of carboxylic and aminopolycarboxylic acids (open symbols) of comparable acidity. This result implies that stronger complexes will be formed at lower pH for the tri-, tetra-, and hexavalent actinide complexes of diphosphonic acids. More efficient stripping of the metal ion from the organic phase will be achieved using such a reagent.

The latter point is demonstrated in Figure 2. By using the thermodynamic data previously determined, the efficiency of various reagents for stripping trivalent actinides from a loaded extractant or resin phase can be predicted. Only the most effective of known reagents are compared in this calculation. Assuming a distribution ratio of 100 in the absence of the complexant, hypothetical

distribution ratios have been calculated as a function of both complexant concentration and acidity. Under all circumstances the diphosphonic acid complexant HEDPA is the most effective stripping agent.

In certain cases, the exceptional complexing ability of 1,1-diphosphonate ligands is indispensable. Research activities of the Chemical Separations group at Argonne has led to the development of a new diphosphonate-containing resin called Diphonix. This new ion exchange resin utilizes the great complexing strength of the 1,1-diphosphonate group immobilized in a polymer matrix. The only water-soluble reagents that can be used to remove the strongly sorbed actinide cations from this resin are the 1,1-diphosphonic acids. An in-house process for removal of radioactive contamination from mixed wastes based on this system is in operation in the Chemistry Division at Argonne. Earlier research activities of the Chemical Separations group led to the development of a uranium-specific separation procedure to remove contamination from natural waters using supported liquid membranes. This process was successful only because of the ability of 1,1-diphosphonic acids to strongly complex uranyl ion.

Current research on these versatile ligands is directed at attaining an in-depth understanding of the relationship between the unique properties of these compounds and their structural features. The principal objective of this research is to attain a degree of understanding adequate to predict a priori the properties of metal complexes simply by knowing the structure of the ligand. Though this research targets specifically f-element complexes, the ligands are of general utility in treatment/isolation procedures for heavy metals. Industrial partnerships are being developed to explore possible applications of these compounds in the water treatment industry.

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Figure 1

Figure 2.

An(III) STRIPPING EFFICIENCY

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