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AQUEOUS COMPLEXES IN f-ELEMENT SEPARATION SCIENCE

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Abstract

Powerful and/or selective extractant molecules/sorbents are a necessary component of an efficient ion exchange or solvent extraction separation process. However, selectivity in extraction and efficiency in process design often rely on reactions occurring in or moderated by the aqueous medium. The focus of this report is on the role of the aqueous phase and reaction that occur in aquo in defining separation efficiency and metal ion selectivity. As our programmatic emphasis is on actinide solution chemistry, the separations chemistry of the f-elements will be used to illustrate the principal role of aqueous chemistry in separation science. Most of the arguments developed apply to metal ion separations chemistry and processes in general. The discussion will consider the application of aqueous complexants, incorporation of aqueous complexants into the extracted complex, and the effect of properties of the aqueous medium on separation efficiency and selectivity. Several historically important separations processes will be considered along with recent efforts in our laboratories to design and characterize new water soluble complexants for improved f element separations.

Introduction:

The process of metal ion separations in both ion exchange and solvent extraction consists, in its most elementary form, of the transfer of a charged metal ion from a polar aqueous phase to an immiscible phase (with different solvating properties) with concomitant charge neutralization. Metal complexation reactions (in both phases), solvation reactions of complexes, metal ions, and complexants, and the general nature of the media all impact the equilibrium condition of the system. Each of these factors can be manipulated to affect the desired phase transfer and recovery, for both transport of the metal ion into the counter-phase and its recovery from that phase are important

considerations in the design of most separation processes. The effectiveness of any separations process is a function of the ability of these reactions to accomplish phase transfer and of the relative affinity of the counter-phase for the species to be separated. Such flexibility derives from the small energy differences required to affect separation. Free energy differences of only 2.7 kilocalories/mole (11.4 kJ/mole), equivalent to the energy associated with one hydrogen bond, are adequate to produce a change in distribution ratio from 0.1 to 10. This example represents a separation factors of 100, implying 99% mutual separation of species in a single contact.

The thermodynamics of both solvent extraction and ion exchange have been extensively discussed and elaborated with elegant arguments previously (1, 2) and so the details of those discussions will not be repeated here. However, an outline of the basic concepts is needed to provide a framework for the following discussion. The equilibria involved in the extraction of a metal ions in a solvent extraction process are shown schematically in Figure 1. The energetics of each of these processes impact the separation equilibrium. Marcus (1) considered metal ion separation by solvent extraction using thermodynamic cycles to demonstrate (not surprisingly) that the principal barrier to extraction of polyvalent cation is the energy of hydration of the cation.

The metal ion typically is present initially in the aqueous medium where the cations are solvated by some number of water molecules. For d-transition metal ions, the number of water molecules in the primary coordination sphere is determined by the strength of orbital overlap between the metal ion and H_2O , crystal field stabilization effects, and cationic charge. Other species (e.g., alkaline earths, rare earths) interact with solvent via ion-dipole forces and their solvation number is determined predominantly by steric factors. In addition to this inner solvation shell, all cations in the aqueous medium organize solvent water in a second coordination sphere, the volume

of which is strongly a function of the charge/radius ratio of the cation. Rizkalla and Choppin (3) suggests that there is a third, disordered zone of water molecules surrounding the ion wherein water structure is intermediate between the ion-dipole ordered structure and the tetrahedral arrangement that represents the bulk solvent. The necessary anions accompanying the cation are typically not strongly hydrated, though O, N, and F engage in hydrogen bonding interactions to modify water structure. Different classes of ions have different effects on the net structure of water (discussed below). Because of the high dielectric constant of H_2O , close association of cations with anions is not required, i.e. free hydrated cations and anions diffuse freely and independently through the solution, though ion pairing is more important at high concentrations of salts. Another consequence of the high dielectric constant of water is that, although charge is conserved in the solution, stable metal complexes may carry a formal charge.

The hydrated cations in the aqueous medium are therefore free to interact with any species present in the aqueous medium. Among the most important species in separations chemistry are water soluble chelating agents. Such species, designated as H_nX in Figure 1, typically exhibit little tendency to distribute into the less polar medium (organic solvent or ion exchange resin). They respond to the acidity and ionic strength of the solution and to the presence of polyvalent metal ions. The species H_nX are ionized forming various anionic species and complexes with the metal ions in the solution. They can also interact with the solvent (H_2O). Besides the chelating agents H_nX , the metal ion may form complexes with the background electrolyte anions (Y^-) and with that fraction of the lipophilic extractant (HL) dissolved in the aqueous medium.

For a target separations problem, there will almost always be multiple metal cations present in the aqueous medium. Water-soluble chelating agents are typically introduced because they

interact more strongly with one metallic component than another. They can therefore be used to control selectivity. This chemistry applies pretty much equally to both ion exchange and solvent extraction separations. It is in fact the basis of the experimental approach to determination of metal complex stability constants in aqueous media by separations methods (4).

The reactions accounting for the transfer of the target metal ion to the counter phase require that the metal ion be "transformed" into a less polar species that is uncomfortable in water. In solvent extraction, the phase transfer reaction is analogous to precipitation (in the sense that a charge neutral compound is formed which leaves the polar aqueous medium). Extractant molecules exhibit some degree of interfacial activity in solvent extraction, as the rate of the phase transfer reactions are mediated by reactions occurring at the solution interface. Interfacial reactions are not relevant to the overall thermodynamics of extraction, but they are of overriding importance in understanding the rates of phase transfer reactions. Aqueous complexants employed in cation separation are typically not surface active.

Basic Equations And Equilibria

The observable parameter governing metal ion separations is the distribution ratio, simply the ratio of the metal ion in the organic (or resin) phase to that in the aqueous phase. For process design purposes, mass transfer must take into account phase ratios, but since the present focus is on the thermodynamics of extraction (rather than process design) the following development of equilibria will always consider the phase ratio to be 1:1 (either by volume for solvent extraction or mass:volume for ion exchange). For all systems, therefore, the distribution ratio is:

$$D = [M]_{\text{org}}/[M]_{\text{aq}} \quad (1)$$

The specific species represented by $[M]_{\text{org}}$ and $[M]_{\text{aq}}$ will be governed by overlapping equilibria in

the aqueous and organic phases. In the following paragraphs, the appropriate equilibria will be described for different classes of separation reactions.

Lipophilic acidic chelating agents which readily exchange H^+ for the target metal ion are one class of ligands. Such reagents may exhibit some aqueous solubility and thus function to a degree as the water soluble chelating agents, but the most effective extractants do not distribute substantially to the aqueous phase. The tendency of such reagents to distribute to the aqueous phase is also a function of the solvating power of the organic medium. The principal equilibria necessary to describe metal ion extraction in such systems are:

The first two equilibria describe the distribution of the extractant between aqueous and organic phases and the acid-base equilibrium of the extractant (which is taken to occur in the aqueous phase). Equation 4 is the principal reaction governing metal ion extraction. The requirement of charge neutrality of the extracted metal complex is met for all extracted complexes, irrespective of the mode of phase transfer. The distribution ratio for the metal ion is described by the equilibrium expression (assuming that HL does not distribute appreciably to the aqueous phase):

$$D = [ML_3]_{org}/[M^{3+}]_{aq} = K_{ex} [HL]^3_{org}/[H^+]^3_{aq} \quad (5)$$

For certain types of extractants (e.g., carboxylic, organophosphorus, and sulfonic acids), dimerization and higher order aggregation of the extractant in the organic phase must also be included in a complete description of the thermodynamics of the system. At high metal loading of the organic phase, the extracted metal complexes tend to aggregate as well.

A second class of extractant molecules are those that accomplish cation phase transfer by solvation of a neutral metal complex. Charge neutrality of the metal complex may be achieved through formation of complexes with simple water soluble anions like nitrate (present either by purposeful addition or as the counter ion for preparation of the initial metal ion solution):

The distribution ratio for the metal ion is defined as:

$$D = [MX_3S_2]_{org}/[M^{3+}]_{aq} = K_{ex}[X^{-}]_{aq}^3[S]_{org}^2 \quad (7)$$

unless X^{-} also participates in complex formation in the aqueous phase in which case $[M]_{aq} = [M^{3+}] + [MX^{2+}] + [MX_2^{+}] + \dots$ and the distribution ratio becomes:

$$D = [MX_3S_2]_{org}/([M^{3+}] + [MX^{2+}] + [MX_2^{+}] + \dots) = K_{ex}[X^{-}]^3[S]^2. \quad (8)$$

Equation 8 can be rewritten in terms of the equilibrium constants for the formation of aqueous complexes, which will be discussed below. Solvating extractants (S) are also known to extract mineral acids from the aqueous phase, and occasionally these equilibria must be taken into consideration in describing the thermodynamics of extraction. Charge neutralization can also be achieved through the agency of an acidic extractant molecule as discussed in the previous paragraph:

Successful combination of a solvating extractant with a chelating extractant results in enhanced extraction efficiency. Such systems are called synergistic, as extraction by the sum of the two is greater than either extractant functioning separately.

A related system is based on the application of ternary or quaternary amine extractants to extract metal ions as ion pairs. With this type of extraction system, the metal ion must associate with

an excess of anions to form an anionic complex:

The distribution ratio for the metal ion is defined as:

$$D = [MX_4A]_{org}/[M^{3+}]_{aq} = K_{ex}[X^{-}]^3[A^{+}X^{-}] \quad (11).$$

This equilibrium expression is also affected by the existence of aqueous complexes MX_n^{3-n} and the ion pairing equilibrium for the extractant. For many d-transition metal ions, the species extracted by amines are the thermodynamically stable (anionic) complexes existing in the aqueous phase in the absence of the lipophilic reagent. For other classes of metal ions (rare earths for example), the extracted anionic complexes often are not important aqueous species. The presence of the amine is necessary to encourage the net phase transfer reaction through formation of the anionic complex. This class of extractants is the solvent extraction equivalent of anion exchange resin and the same equilibria describe both.

A fourth class of extractant molecules, comparable to cation exchange resins, are surfactants. These extractants are strongly acidic and highly aggregated in the organic phase forming reverse micelles which sequester the extracted metal ions in the hydrophilic inner region of the reverse micelle. Their metal ion extraction equilibria are comparable to those of acidic extractants except that the stoichiometry with respect to the analytical concentration of the extractant is typically reduced to a nominal 1:1 with the micelle performing the role of the extractant. Charge neutralization is attained by the expulsion of H^{+} (or other monovalent cation e.g., Na^{+}) from the micelle. Such extractants exhibit good selectivity for metal ions of significantly different properties (e.g., oxidation state/formal charge) but almost none for cations with similar properties.

Of these four general classes of phase transfer reactions, only those systems involving the application of lipophilic chelating agents exhibit any inherent tendency toward cation selectivity for cations like the trivalent lanthanides. Solvating extractants (e.g. tributyl phosphate, TBP), ion pair forming extractants (e.g., quaternary amines), and micelle forming extractants typically extract a given class of metal ions indiscriminately (though they are sensitive to the oxidation state of the metal). Such reagents (and their ion exchange resin equivalents) must rely on changes in aqueous chemistry for selectivity. In effect, such systems serve as "platforms" for selective separations based on differences in the aqueous chemistry of the system. The variation in aqueous chemistry may involve changes in the oxidation state of the metal ion, complexation, or more subtle alteration of the aqueous medium.

As a production-scale separation process is typically operated in a stage-wise manner, the extraction equilibria are readjusted to transfer the metal ion back to a "clean" aqueous solution thus separating the metal ion from the contaminants present initially and the extractant solution/resin. The recovered metal ion can then be transformed by (for example) precipitation or electrowinning to produce the final purified material. This process creates additional opportunities to increase the purity of the recovered metal ion. In most production-scale processes, it is desirable to recycle the extractant solution/resin. Clean up of these materials is typically done relying on contact with an appropriate aqueous solution (analytical separations do not ordinarily employ such processes because the small scale reduces the requirement for recycle of expensive reagents). The focus of the following discussion will be on the various ways in which changes in the composition of the aqueous medium effect extraction efficiency and selectivity in metal ion separations.

Early Separations of f-Elements

To elaborate the role of the aqueous solution on the separation of metal ions, the f elements provide a particularly relevant framework for discussion. Their chemistry is diverse providing an opportunity to examine a variety of different aspects of metal ion separations while narrowly focusing on a particular class of metal ions. At the same time, the similarity of the chemical behavior of trivalent actinides and lanthanides represents a severe test of the viability of any separation scheme. It is also particularly appropriate to pursue this discussion based on the chemistry of lanthanides and actinides since no class of metal ions owes more to modern separation science. The availability of macroscopic amounts of pure lanthanides for technological applications and our knowledge of the properties of the actinides relies heavily on ion exchange and solvent extraction separations, as the following discussion will illustrate.

Fractional crystallization is the most straight forward solid-liquid separation method and was the technique of choice in the early days of the investigation of the chemistry of the lanthanides. But the separation of individual lanthanide ions by this method relied on extremely small differences in solubility which therefore demanded hundreds or even thousands of repetitions to achieve useful separations of the elements (5). The introduction of first ion exchange and later solvent extraction procedures greatly increased capacities for the production of individual lanthanides and ultimately made their practical application possible.

Our present state of knowledge regarding the basic science of the actinides is even more intricately bound to their separations chemistry. The work of Becquerel and the Curies that led to the discovery of radioactivity and new elements relied heavily on precipitation techniques. The discovery of fission and the production of the first transuranic elements likewise required physical separation methods to isolate small amounts of radioactive metals from complex matrices. Most

separations were based on precipitation, though ether extraction of selected metal complexes also figured prominently.

During World War II and for more than 40 years after, plutonium production was accomplished at the Hanford site on the Columbia River near Richland, Washington (6). The isolation of plutonium from uranium and fission products was initially accomplished by precipitation with BiPO_4 . The process, pioneered by S. G. Thompson, involves coprecipitation of Pu(IV) by BiPO_4 followed by oxidation to Pu(VI) , which redissolves from the BiPO_4 matrix. This process was soon replaced by solvent extraction processes based on the use of methyl(isobutyl)ketone (REDOX Process) and later tributyl phosphate (PUREX Process). PUREX remains the principal method for processing spent reactor fuel today.

Following the discovery of neptunium and plutonium in 1940, a major research effort was launched to synthesize and determine the properties of the transplutonium elements. Seaborg proposed that these elements represented the 5f series, analogous to the lanthanides, and headed a team that synthesized and characterized the remaining 9 members of the series over the period of 1944 - 1961. The irradiation methods used to produce the transuranium elements are always accompanied by some fission. Most important among fission products from a separations perspective are lanthanides, whose solution chemistry closely resemble that of transplutonium actinides. Identification of the new transplutonium elements therefore required efficient separations methods not only for actinides from actinides but also for actinides from lanthanides. Several of these techniques will be discussed below.

f-Element Solution Chemistry

To facilitate the following discussion, a brief overview of the solution chemistry of f

elements will be useful. The predominant stable oxidation state for lanthanide ions is the trivalent. Only Eu^{2+} and Ce^{4+} , potent reducing and oxidizing agents respectively, are typically encountered in "normal" aqueous solutions. Because the spatial extension of the 4f (and 5f) valence orbitals is slight, addition of valence electrons cannot effectively shield the increasing nuclear charge as the atomic number increases across the series. As a result, the ionic radii of the trivalent cations decrease more-or-less regularly (by about 20%) from La to Lu. The trivalent radii of actinides behave similarly with r_{Am} r_{Nd} . This is an important characteristic in the separations chemistry of f elements.

For the elements with $Z > 94$ (except for nobelium, $Z=102$), the trivalent oxidation state is the most stable, although Am(V) and Bk(IV) have been utilized in separations in basic systems. Therefore, the solution chemistry of the transplutonium elements strongly resembles that of the trivalent lanthanides. For thorium, only the tetravalent oxidation state is important. For U, Np, and Pu, the redox chemistry is varied and different oxidation states are of use in separation schemes. The lower oxidation states (III and IV) exist as hydrated cations in aqueous solutions while the upper oxidation states (V and VI) are linear dioxocations having formal +1 and +2 charges. In general, acidic solutions favor lower oxidation states while basic media promote the stability of the higher states. In actinide processing the most important species are U^{4+} , UO_2^{2+} , Np^{4+} , NpO_2^+ , NpO_2^{2+} , Pu^{3+} , Pu^{4+} , PuO_2^{2+} , Am^{3+} and Cm^{3+} , though the hexavalent oxidation states of Pu and Np are moderately strong oxidants. The middle oxidation states (IV and V) of U, Np, Pu, and Am are prone to disproportionation at moderate concentrations in acidic solutions. The multiplicity of readily available oxidation states for these elements is of major significance in their process chemistry.

Lanthanides and actinides (in all oxidation states) form weak complexes with halides

(except F^-) and moderate to strong complexes with oxygen donor ligands like aminopolycarboxylates and polycarboxylic acids. The relative order of complex stability is typically $An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^+$, though chelating agents with unfavorable coordination geometries can reduce the relative stability of AnO_2^+ and AnO_2^{2+} complexes. The coordination numbers for these ions in solution are variable, reflecting the strongly ionic nature of the bonding and the general absence of directed valence effects: 9-12 for An^{4+} , 7-9 for An^{3+} , and 4-6 for $AnO_2^{+/2+}$ (axial coordination only). They are strongly hydrated in aqueous solutions and readily hydrolyzed (hydroxides precipitate at pH 1 for An^{4+} , pH 5 for AnO_2^{2+} , pH 7 for An^{3+} , pH 9 for AnO_2^+). The actinides exhibit a slightly greater tendency to interact with soft donor atoms (sulfur, chloride, nitrogen) than analogous lanthanides. The redox chemistry, solvation effects, and strength of soft donor interactions all are important in the separation chemistry of these elements.

To affect a mutual separation of individual actinides lighter than Am, or of these metal ions from the lanthanides, separation systems sensitive to the oxidation state of the metal ion is all that is required. The above mentioned REDOX and PUREX processes achieve good selectivity for Pu and U through the simple expediency of oxidation state control. For example, in the PUREX process, Pu(IV) and U(VI) are extracted from nitric acid. Stripping of Pu is accomplished by reduction with Fe^{2+} or U^{4+} .

For the transplutonium elements, more subtle differences between metal ions must be employed for a successful separation as the dominant oxidation state is the trivalent. The decreasing cation radii with increasing atomic number and the slightly greater affinity exhibited by actinide cations for soft donor ligands forms the basis for these separations. The latter characteristic is the central determinant in the separation of the groups (actinides from lanthanides). The shrinking

cation radius and the concordant increase in the interaction strength (largely electrostatic in nature) of these metal ions with ligand donor atoms forms the basis of the separation of individual members of the respective series. The multiple interactions involved in the phase transfer process limit the predictability of this effect, as will be discussed below.

In the following section, the impact of chemical processes occurring in the aqueous phase on the separations chemistry of lanthanide and actinide ions will be presented. It is intended that the generic role of those reactions in metal ion separations will emerge from this discussion. The results reported will include both historically important processes and the results of research in our laboratories on the search for greater understanding of these phenomena and new reagents for improvements in the efficiency of f-element separations with emphasis on process chemistry.

Medium Effects and Solvation

Choppin and coworkers (7) have investigated the effect of various solutes on the hydrogen bonded structure of water. Their studies considered the impact of electrolyte composition and concentration, and that of non aqueous solvents on the hydrogen bonded structure of water. Infrared spectroscopic data were interpreted in terms of the number of hydrogen bonds to individual water molecules. Liquid water can be considered to consist of molecules having 0, 1, or 2 water molecules hydrogen bonded to the protons. A higher percentage of more highly hydrogen bonded species implies greater three dimensional structure in the solvent. The energetics of the fit of the metal ion into this structure constitutes an entropy contribution to the overall extraction reaction.

The solutes which make up aqueous solutions can either promote or disrupt the 3-D structure of water. Hydrogen ions (H^+) and hydroxide ions (OH^-) are the ultimate structure makers in aqueous solutions, as they fit perfectly into the water structure. Therefore, pH must have an effect on water

structure, at least at the extremes. Various water miscible solvents (e.g., methanol, ethanol, acetone, DMSO) have a more-or-less predictable effect on the structure of water. Small, hard sphere metal cations tend to promote order in the solution while large cations tend to disrupt the structure. Among typical anions, fluoride is a strong structure maker, sulfate, phosphate, and nitrate less efficient structure makers, while the heavy halides and thiocyanate disrupt the water structure. Among anions typically encountered in separations, the most effective at disrupting water structure is perchlorate. Though such effects are difficult to quantify, the observation of a perchlorate effect is very likely the result of a more favorable net entropy contribution growing out of the structure breaking nature of the anion. Though this effect increases overall extraction efficiency, its effect on separation factors is more difficult to predict.

Lincoln (8) has discussed both the rates and the solvation numbers of the lanthanide cations, observing that there is a great variety in both solvent exchange rates and coordination numbers in non-aqueous media. The kinetic parameters for water exchange (9) are consistent with a concerted associative mechanism, (dependent on $[H_2O]$) characterized by rapid exchange. Partial substitution of non-aqueous solvents for water results in a net decrease in the hydration of the cation, thereby reducing the energetic requirements for desolvation and promoting phase transfer. Several critical early investigations of the chemistry of actinides relied heavily on this effect for separation of lanthanides from the transplutonium actinides.

Beginning with the work of Street and Seaborg (10) in 1950 and followed by Diamond, Street and Seaborg (11) in 1954, methods for the separation of trivalent actinides from lanthanides by ion exchange techniques were developed. These authors found that below 6 M HCl, trivalent actinides and lanthanides eluted from a cation exchange column together. At concentrations of HCl

greater than 6 M HCl, actinides were eluted from the column while the lanthanides were retained. Diamond et al offered a reasonable argument that behavior of Pm^{3+} in this system was "normal", that is the distribution ratio should level off or increase slightly due to changes in the internal structure of the resin phase as acidity increases beyond 6 M. The observation of steadily decreasing distribution ratios for Am^{3+} were taken to indicate the existence of more stable Am-Cl complexes based on a covalent interaction between Am^{3+} and Cl^- (specifically involving the participation of the 5f valence orbitals of Am). Recent examination of actinide/lanthanide complexation has failed to establish a thermodynamic basis for a covalent component in actinide bonding to soft donor atoms. The lack of such proof should not be too surprising as the covalent contribution is likely to be less than 10% of the total bond strength (under the best of circumstances), the energy differences are slight, and cation hydration (for which there is minimal likelihood of a covalent contribution) dominates the thermodynamics of these systems.

An alternative approach to reducing the energy required to accomplish partial dehydration of the cation (and hence allow the actinide ions to interact more strongly with weak ligands like Cl^-) is to substitute a weaker solvent for a portion of the water comprising the solution. Street and Seaborg (10) reported that group separation of the lanthanides and trivalent actinides could be achieved by cation exchange eluting with 20% ethanol saturated with HCl. The presence of the alcohol enhances the difference in chloride complex stability between the lanthanides and actinides as a result of partial dehydration of the cation in the 20% ethanol solution. Development of processes based on partial substitution of ethanol, acetone or acetonitrile for water in both cation and anion exchange continues today.

Anion exchange employing either lithium chloride or ammonium thiocyanate were reported

as efficient methods for the separation of lanthanides from trivalent actinides. SCN^- coordinates with the actinide through the harder N atom (rather than S), and so much lower concentrations are needed than are required for LiCl. The actinides are preferentially sorbed by the anion exchange resin due to stronger complexes with Cl^- leaving the lanthanide ions in the aqueous solution. This separation has technological importance as LiCl anion exchange separation of trivalent actinides from lanthanides, is the critical step in the production of transamericium elements for research purposes at the Radiological Engineering Development Center (REDC) at ORNL.

Remembering the A-B-C zone model for cation hydration discussed above, a simple calculation reveals how high salt concentrations contribute to this separation. In 10 M LiCl (density = 1.1812 g/cc, 8.24 molal solution, CRC Handbook of Chemistry and Physics, 67th edition) the nominal water concentration is reduced to 36.1 molal. However, if we also consider that the lithium ion is a tetrahydrate cation in aqueous solution the "free" water concentration is reduced to only 3.2 molal. The chloride ion, also 8.24 molal, tends to promote the disordered C zone to further disrupt the normal hydrogen bonded structure of water. The polyvalent lanthanide and actinide cations, which are present at very low concentrations, thus are surrounded by fewer and less organized free water molecules. As a result of the decreased hydration, Cl^- can compete more favorably for the available cation coordination sites and the stronger soft-donor interaction of the actinide is manifested.

An additional phenomenon related to the effect of the anion on water structure is a so-called "perchlorate effect" (12). It has been often observed that extraction of metal ions from perchlorate media is greater than that from equivalent nitrate or chloride solutions (independent of the class of extractant). In the case of separations based on solvating extractants (e.g., TBP), it is at first glance

surprising that lanthanide/actinide extraction should be stronger from perchlorate than from nitrate media, as the former are very weak ligands while the latter complex these ions much more efficiently. An explanation for the phenomenon, and for the relative ease of extraction of metal ions from salt solutions (relative to that from equivalent acids or from mixed aqueous media), may lie in the effect of the solutes on water structure.

The results reported by Sekine (13) show the combined effect of soft-donor ligands and of perchlorate on Am/Eu separation using a solvating extractant. The extraction/separation of americium and europium with 5% TBP/hexane from 5.0 M NaClO₄/NaSCN, and from NaSCN solutions without supporting electrolyte (pH 4-5) exhibit strong dependence on the concentration of SCN⁻ (Figure 2). In the absence of perchlorate, the separation factors are higher at low thiocyanate concentrations, though distribution ratios are low. At constant ionic strength (5.0 M), the trend is reversed, i.e., separation factors (S_{Eu}^{Am}) are higher at higher concentrations of SCN⁻. Distribution ratios are dramatically higher in the presence of perchlorate. The free energies for extraction of both Am and Eu is 12-17 kJ/mol more favorable in the presence of perchlorate (at a given [SCN⁻]). At the highest SCN⁻ concentrations, separation factors are about unity because the disrupting effect of SCN⁻ and ClO₄⁻ on the water structure essentially eliminate the effect of the soft-donor interaction in actinide binding to the SCN⁻.

Thiocyanate has been used for an actinide/lanthanide separation based on the use of a quaternary amines immobilized on an inert support to create extraction chromatographic materials which combine the best features of the extractants with the increased efficiency of extraction chromatography. Horwitz et al (14) have reported the application of the thiocyanate effect for the selective separation of actinides from lanthanides using such resins. When loaded from a solution

1.0 M NH_4SCN /0.1 M HCO_2H , trivalent actinides (represented by Am^{3+}) are quantitatively sorbed while lanthanides (from La to Eu) are rejected. Am can be eluted from the column with 0.25 M HCl for a very selective separation.

One of the most interesting examples of a medium effect in liquid-liquid separations of f elements are the so-called "aqueous biphasic" systems. Polyethylene glycols have been demonstrated to partition from concentrated aqueous salt solutions. The effect relies heavily on the ability of certain salts to order the structure of water. Nitrate, sulfate, carbonate, and hydroxide are particularly effective in this role. A key characteristic of these systems is that the immiscible phases are still largely aqueous in nature. Myasoedov and coworkers have reported conditions for the separation of transplutonium elements from uranium, thorium and lanthanides (15). The aqueous biphasic itself does not extract actinides strongly, but Arsenazo III is a highly effective carrier for these metal ions. There are similarities between this concept and the altered state representing the internal structure of ion exchange resins.

Aqueous Complexation in Lanthanide/Actinide Separations:

Medium effects of the type described above typically have their greatest impact on enhancement of extraction efficiency by reducing the dehydration energy barrier to phase transfer. The enhanced selectivity observed in lanthanide/actinide group separations from Cl^- and SCN^- solutions rely on the combined effects of reduced hydration energy and complex formation. The role of aqueous complexation in f element separations will now be considered in more detail.

For the simplest case in which the aqueous metal complexes are not extracted into the counter phase, the observed distribution ratio represents a balance between the two phase extraction reaction, and the homogeneous complexation equilibria in the aqueous phase. If we return to the

earlier example of an acidic chelating extractant, the distribution ratio for trivalent metal ion extraction in the absence of aqueous complexation reactions is governed by the equilibrium shown in equation 4. The thermodynamic equilibrium constant for this reaction must include activity coefficients. Activity coefficients are seldom known with sufficient accuracy for their inclusion in a description of the thermodynamics of separations. It is expedient for this discussion to consider equilibrium quotients in which activity coefficients are considered to be constant and invisibly lumped into the equilibrium quotient. Providing that a standard state is defined and maintained, such a simplification is ordinarily justified. Introduction of a water soluble complexing agent caused a redistribution of the metal ion among the extracted complex (ML_3), the free metal ion (M^{3+}) and the various water soluble complexes (MX_n). Assuming that the aqueous complexant does not participate in the phase transfer reaction, the distribution ratio is:

$$D = [ML_3]_{org} / ([M^{3+}] + [MX^{2+}] + [MX_2^+] + \dots) \quad (12)$$

which can be rewritten in terms of the homogeneous (aqueous) phase equilibrium reaction for complex formation as:

$$D = [ML_3]_{org} / ([M^{3+}](1 + \beta_1[X^-] + \beta_2[X^-]^2 + \dots)). \quad (13)$$

In equation 5, the ratio $[ML_3]_{org}/[M^{3+}]_{aq}$ was established as equivalent to $K_{ex} [H^+]^3/[HL]^3$ for the case of an acidic extractant, so:

$$D = K_{ex} [HL]^3/[H^+]^3 / (1 + \sum \beta_i [X^-]^i). \quad (14)$$

The object of most metal ion separations processes is to isolate one metal ion from several related species. The separation factor for mutual isolation of two metal ions is a measure of the effectiveness of the separation process at accomplishing the separation. It is defined as the ratio of the respective distribution coefficients (D's) or,

$$S_{m'}^m = \frac{D^m}{D^{m'}} = \frac{K_{ex}^m / (1 + \sum(\beta_i^m[X]^i))}{K_{ex}^{m'} / (1 + \sum(\beta_i^{m'}[X]^i))} \quad (15).$$

$([HL]^3/[H^+]^3)$ terms cancel providing the target metal ions are extracted with the same stoichiometry - if the extraction stoichiometries differ, the separation factor will be a function of acidity and extractant concentration as well). The separation factor for the two metal ions is therefore directly proportional to the relative extraction efficiency of the metals ($K_{ex}^m/K_{ex}^{m'}$), but inversely proportional to the relative stability of the aqueous complexes, though potentially in a complex fashion. It is further possible to include a second aqueous complexant to enhance the difference between the two metal ions. An example of such a system will be presented below.

According to equation 15, the most effective separations will be achieved in those systems in which the target metal ion interacts more strongly with the extractant HL but is complexed less strongly by the aqueous ligand X. The need for complementarity of extractant and complexant has been illustrated in a previous study of the effect of the water-soluble phosphonate complexant phosphonoacetic acid (PAA) on Am/Eu separation from three different extraction platforms: an acidic extractant (bis(2-ethylhexyl) phosphoric acid - HDEHP), a micellar extractant (dinonylnaphthalene sulfonic acid - HDNNS), and a neutral bifunctional extractant (octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide - CMPO) from nitrate and thiocyanate media (Table 1).

In the case of HDEHP, Eu is extracted about 30 times more efficiently than Am ($\log K_{ex}^{Eu} = -1.06$, $\log K_{ex}^{Am} = -2.61$, $S_{Eu}^{Am} = 0.028$ after correction for nitrate complexes). Since the Eu-PAA complexes are more stable than those of Am, the extractant and complexant ligands in this system work in the opposite sense resulting in lower separation factors when the complexant is present than

Table 1. Americium/europium separation factors for extraction from nitrate/thiocyanate solutions in the presence of phosphonoacetic acid (pH 2).

Extractant	[PAA]	[SCN ⁻]	[NO ₃ ⁻]	S _{Eu} ^{Am}
HDEHP	0.0	0.0	0.5	0.032
HDEHP	0.2	0.0	0.5	0.051
HDNNS	0.0	0.0	0.5	0.83
HDNNS	0.24	0.0	0.5	1.67
CMPO (0.1 M)	0.0	0.0	0.5	0.77
CMPO (0.1M)	0.2	0.0	0.5	1.43
CMPO (0.5 M)	0.0	0.0	0.5	1.03
CMPO (0.5M)	0.2	0.0	0.5	2.07
CMPO (0.05 M)	0.0	0.5	0.0	5.9
CMPO (0.05 M)	0.2	0.5	0.0	24.2

when it is absent and the PAA thus reduces the separation efficiency. In HDNNS/toluene as the extractant, the separation factor was $S_{Eu}^{Am} = 0.83$ in the absence of PAA and $S_{Eu}^{Am} = 1.81$ for extraction from 0.34 M PAA at $[H^+] = 0.02$ M and 0.5 M NaNO₃. Similarly, neutral bifunctional extractants like CMPO exhibits little lanthanide/actinide selectivity when extracting these metal ions from nitrate media ($S_{Eu}^{Am} = 1.03$). When 0.2 M PAA is introduced into the aqueous phase, the

separation factor increases to $S_{Eu}^{Am} = 2.07$, which is consistent with calculations based on the respective aqueous stability constants of Am^{3+} and Eu^{3+} (16).

With thiocyanate as the counter ion americium is preferentially extracted and the separation factor S_{Eu}^{Am} is about 7 (17). As the Eu complexes are more stable than Am, both the D_o^{Am}/D_o^{Eu} and $(1+\Sigma\beta_{mhl}[H^+]^h[L^{3-}]^l)_{Eu}/(1+\Sigma\beta_{mhl}[H^+]^h[L^{3-}]^l)_{Am}$ terms of equation 15 are favorable. For extraction from 0.1 or 0.2 M PAA/0.5 M KSCN, pH 2, the separation factors increase to 12 and 15 respectively. This system has been applied to determine a separation factor for Am over the entire lanthanide series ranges between 9 to 25, as shown in Figure 3. This combination has been validated for both solvent extraction and extraction chromatographic separations.

There are important examples from the literature that demonstrate the effect of aqueous complexants on f element separations. In the nucleosynthesis of transplutonium elements, actinides were separated from trivalent lanthanide fission products using chloride or thiocyanate ion exchange as described above. Another system useful for group separations is TALSPEAK (Trivalent Actinide Lanthanide Separation by Phosphorus Reagent Extraction from Aqueous Komplexes) (18). This extraction system is based on the use of acidic organophosphorus extractants (like HDEHP), which is an excellent reagent for separation of individual trivalent lanthanides/actinides from a mixture (Figure 4a). Weaver and Kappelmann (18) reported that replacement of the mineral acid solution used in the intragroup separation with various carboxylic acids, and mixtures of carboxylic and aminopolycarboxylic acids results in a very satisfactory group separation. Extraction from 1 M carboxylic acid (pH 1.8) solutions depresses the extraction of Am relative to the lanthanides. At higher pH's (≈ 3) the separation factors are increased, with the most consistent enhancement observed for lactic acid. Addition of only 0.05 M DTPA to the solutions of

carboxylic acids at pH 3 resulted in dramatically improved separation factors. For extraction from 1 M lactic acid/0.05 M DTPA/pH 3 with 0.3 M HDEHP/diisopropylbenzene (DIPB), the worst actinide/lanthanide separation factor is for $SF^{Nd}_{Cf} \approx 10$ (Figure 4b).

The combination of water-soluble chelating agents and cation exchange for phase separation led to the development of the first efficient separations methods for isolation of transplutonium elements (19). Am, Cm, Bk, Cf, Es, and Fm were eluted in reverse order from Dowex 50 cation exchange resin when the eluting solution was 0.25 M NH_4 (citrate) at pH 3.0-3.5 or 0.4 M NH_4 -lactate at pH 4.0-4.5. Aminopolycarboxylic acid ligands like EDTA also demonstrated good separation factors but suffered from slower equilibration rates. Because transuranic actinides were often produced a few atoms at a time and had unknown properties, fast separations techniques with predictable behavior were required. More selective separations with better kinetics were observed with the introduction of α -hydroxyisobutyric acid (20), which provides average separation factors for adjacent lanthanides or trivalent actinides of about 1.3-1.5. In these systems, separation is achieved almost solely as a result of the difference in stability of the aqueous complexes of the metal ions.

One might guess that since the lanthanide cationic radii change so consistently across the series that there might be a variety of chelating agents as effective as α -hydroxyisobutyric acid for accomplishing the isolation of individual lanthanide ions. Examination of the extensive database of critically evaluated stability constants for lanthanide complexes reveals that the aqueous chemistry of the system is much more complex (and there are in fact very few systems that exhibit as consistent a trend). This fact becomes abundantly clear in a comparison of the relative free energy of complexation of lanthanide complexes with a series of potentially useful ligands.

In Figure 5a is shown the relative stability of a variety of lanthanide complexes (normalized to La^{3+}) with several carboxylic acids for which stability constants are known. The free energies for formation of complexes of lanthanides with acetate, oxydiacetate, and citrate show regular changes in lanthanide stability between La and Nd but are independent of radii or even reverse for complexes of the heavier lanthanide ions with some ligands. The relative free energies for α -hydroxyisobutyric acid are remarkably consistent across the series, which explains its unique behavior in trivalent f-element separations. The structurally restricted analog for ODA (THFTCA) exhibits greater selectivity from La to Dy, but is not effective beyond Dy. However, thermodynamic data suggest that this selectivity is less pronounced in the corresponding 1:2 complexes (21). The relative free energies of lanthanide aminopolycarboxylate ligands (Figure 5b) change more consistently with cation radius than the polycarboxylates. Calculated separation factors for the structurally restricted ligands DCPA (as compared with NTA) and DCTA (compared with EDTA) offer steeper slopes than their non-constrained analogs. The planar arrangement of donor atoms in dipicolinic acid is apparently not favorable for lanthanide separations.

Because there are substantial amounts of actinides present in alkaline media in underground storage tanks at former actinide production facilities, there has been some focus on the development of separations techniques for actinides in alkaline solution. Under these conditions, water soluble chelating agents are required to maintain solubility of the readily hydrolyzed actinide cations. Such separations have been reviewed by Karalova et al (22). Both solvating and chelating extractants have been used in these studies. Primary and quaternary amines, alkylpyrocatechols, β -diketones, pyrazolones, and N-alkyl derivatives of aminoalcohols are the extractants indicated as useful for alkaline extraction processes. The aqueous complexing agent employed include EDTA, DTPA and

DTPMPA - diethylenetriamine-N,N,N',N'',N''-pentamethylenephosphonic acid. The separation factors are based mainly on the difference in the rates of the metal complexation equilibria for Eu and Am. Such kinetic-based separations represent a dramatically new approach to metal ion separations.

Recent Results on New Reagent/Process Development

Our research on the coordination complexes of f elements with derivatives of methanediphosphonic acid (16, 23-26) has established that these complexing agents are very efficient general stripping agents for actinide processing. Stability constants for Eu(III) (23), Cm(III) (24), Am(III) (16), Th(IV) (25) and U(VI) (26) complexes with a wide variety of substituted diphosphonic acids have been measured using solvent extraction distribution methods. We have also investigated certain aspects of the kinetics of their complexation reactions for potential application in separation. Thermodynamic results and laser-induced fluorescence decay studies of europium complexes strongly suggest intramolecular hydrogen bonding contributes to the unusual stability of the f element complexes in acid solutions (27). Our research effort has also established that diphosphonate complexing agents can be designed to be readily decomposed by mild treatment to facilitate waste disposal (28). We have also suggested an approach to oxidation state-specific separation of actinides within the general framework of TRUEX solvent extraction through application of diphosphonates in the stripping stage. The CMPO/SCN/PAA separation of Am from lanthanides described above is another example of a separation enhanced by the application of phosphonate complexants.

The TRUEX process for extraction of actinides and lanthanides is now a well-known and accepted technology for total actinide recovery (29). More recent research has led to the

development of the SREX process for extraction of Sr^{2+} (30). This solvent extraction process employs the crown ether extractant di(t-butyl cyclohexano) 18-crown-6 as the Sr selective extractant with n-octanol as the organic diluent. These two solvent extraction systems function in a complementary fashion when the diluent system is a normal paraffin hydrocarbon with a simple phosphonate or phosphate ester is present as a phase modifier. This combined process solvent will efficiently extract lanthanides, actinides and strontium from nitric acid solutions.

One ubiquitous component of typical radioactive waste streams which does not require burial in a geologic repository is uranium. By virtue of the low specific activity of its principal isotopes ($\text{SA}^{(238\text{U})} = 0.746 \text{ dpm}/\mu\text{g}$, $\text{SA}^{(235\text{U})} = 4.80 \text{ dpm}/\mu\text{g}$), uranium could be safely disposed of in near surface burial using a concrete waste form. However, the stable oxidation states of uranium (U(IV) and U(VI)) are both strongly extracted by CMPO from nitric acid solutions. Selective separation of uranium from trivalent and tetravalent actinide cations is highly desirable. However, UO_2^{2+} extraction is typically intermediate between that of the trivalent and tetravalent actinides so selective separation must rely on the use of a reagent which can distinguish the unique geometry of the linear dioxouranyl cation.

Such a separation system has been identified (31). The extractant solution combining octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) for actinide extraction, diamyl(aryl) phosphonate (DA(A)P) for enhanced phase compatibility, and di(t-butyl cyclohexano) 18-crown-6 for Sr^{2+} extraction in Isopar L is designed for complete removal of radioactivity from nuclear wastes. The aqueous complexant, tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA) (as the disodium salt), provides the desired separation of UO_2^{2+} from the other actinides. Effectively, THFTCA complexes An(III) and An(IV) holding them in the

aqueous phase while UO_2^{2+} is extracted by CMPO. Extraction of trivalent, tetravalent and hexavalent actinides by CMPO from HNO_3 and from THFTCA are shown in Figure 6a and 6b respectively. Studies of the thermodynamics of complexation of uranyl and lanthanide complexes with THFTCA suggest that anomalously weak complexes are formed between UO_2^{2+} and THFTCA to account for the unusual selectivity of this system.

Conclusions

In the above discussion, numerous examples have been given along with a theoretical framework to illustrate the impact of the composition and characteristics of aqueous media on metal ion separations. Though the discussion has emphasized separations of f elements, most of the concepts presented apply with minor modifications to metal ion separations in general. These observations for the most part apply equally to separations based on liquid-liquid extraction, ion exchange, extraction chromatography, and membrane-based processes. They serve to illustrate that the low energetic requirements of a selective separation offer many opportunities to achieve a desired separation, and that great flexibility can be gained through modifications of the aqueous medium.

Areas for emphasis in future research include the following: design of aqueous complexants capable of distinguishing the size and shape of cations, improved understanding of solvation phenomena in both aqueous and mixed aqueous/organic media, development of aqueous complexants that do not create environmental hazards or waste disposal complications when their utility is concluded, and kinetics of metal ion complexation processes both in homogeneous solutions and at interfaces. Objectives specific to actinide/lanthanide separations include the design of new soft-donor or mixed hard-soft donor ligands (both water soluble and lipophilic species) to

enhance lanthanide /actinide separations. Many of these suggested research areas require a serious commitment to fundamental research in coordination chemistry.

Figure Captions:

Figure 1. Schematic representation of pertinent equilibria in solvent extraction processes.

Figure 2. Solvent extraction separation of americium and europium using 5 % tributyl phosphate in hexane from NaSCN and 5.0 M NaSCN/NaClO₄ mixtures at pH 4-5 (Reference 13).

Figure 3. Separation of Am³⁺ from the lanthanides by a mixture of CMPO and TBP in Isopar L from a solution containing 0.5 M NaSCN and 0.2 M phosphonoacetic acid at pH 2.

Figure 4. a.) Distribution ratios for trivalent lanthanide and actinide extraction by HDEHP/toluene from aqueous nitric acid solutions, b.). Distribution ratios for trivalent lanthanide and actinide cations by 0.3 M HDEHP/diisopropylbenzene from 1.0 M lactic acid/0.05 M DTPA at pH 3 (TALSPEAK).

Figure 5. Relative free energies of lanthanide complexes with a) polycarboxylic acids and b) aminopolycarboxylic acids (normalized to La³⁺).

Figure 6. a) Extraction of trivalent, tetravalent and hexavalent actinides by TRUEX Process Solvent (0.2 M CMPO/1.2 M TBP/dodecane b) Extraction of trivalent, tetravalent and hexavalent actinides by the Combined Process Solvent (0.2 M CMPO/1.2 M DA(A)P/0.05 M di-tBuCh18C6/Isopar L from 0.05 M Na₂THFTCA/HNO₃.

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Chemical Processes in Solvent Extraction

Organic Solution

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