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AQUEOUS COMPLEXES IN SEPARATIONS OF f-ELEMENTS: OPTIONS AND STRATEGIES FOR FUTURE DEVELOPMENT

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ABSTRACT

Powerful and/or selective extractant molecules/sorbents are a necessary component of efficient metal ion separation processes. However, selectivity in extraction and efficiency in process design often rely on reactions occurring in or moderated by the aqueous medium. This report describes the role of the aqueous phase and reactions that occur in aquo in defining separation efficiency and metal ion selectivity. As our programmatic focus is on actinide solution chemistry, the separations chemistry of the f-elements will be used to illustrate the principal role of aqueous chemistry in metal ion separations. Most of the arguments developed apply to metal ion separations chemistry and processes in general. The discussion will emphasize the role of complexation and the effect of properties of the aqueous medium on separation efficiency and selectivity. 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.

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INTRODUCTION

The process of isolating individual metal ions from mixtures of metallic and nonmetallic components by treatment of aqueous solutions can be both chemically and technologically complex. For analytical-scale separations, the principal requirement is for a phase transfer process that exhibits high efficiency for the target metal ion over competitors. These systems often are quite demanding requiring high single stage efficiency. Because of the small scale (in terms of materials), recovery and reuse of expensive extraction reagents is seldom needed. In production-scale hydrometallurgical processes, single stage efficiency is not as important as ready recovery of the target metal (i.e., reversibility of the separation reaction) and the ability to recycle the phase transfer reagent. In such applications, enormous amounts of chemical reagents (extractants, resins) typically are required. The two extremes impose different demands upon the chemical system, and the systems must be adjusted to accommodate the chemistry of both the target and the contaminants.

One of the practical advantages accruing from the complexity of most hydrometallurgical processes is the large variety of chemical equilibria that can be manipulated to fine-tune the separation. While selective extractants/adsorbents can provide great advantages in cation-specific separations, often success or failure is based on the nature of the aqueous medium. The subject of this report is the effect of reactions occurring in the aqueous medium on cation specificity and selectivity in hydrometallurgical processing. The principal emphasis will be on solvent extraction because such reactions provide more diverse opportunities to refine the system. However, most of the concepts discussed apply equally to ion exchange and membrane-based separations.

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 owe more to modern separation science [1]. The availability of macroscopic amounts of pure lanthanides for technological applications and our knowledge of the properties of the actinides is closely tied to development of ion exchange and solvent extraction separations. In the post-Cold War era, the science and technology of these separations can have enormous impact on the cleanup and decommissioning of the now idle nuclear weapons complex.

The following discussion will include enough of the basic chemistry of f-element separation science to provide background for interpretation of historically significant separation processes, and to elaborate present trends and potential future directions for research on the aqueous separations chemistry of these elements. The demands of process-scale (as opposed to analytical-scale) separations will be emphasized.

Basic Hydrometallurgical Process Chemistry

For most metal ion separation problems, the principal task will be selective isolation of a single metal ion or group of metal ions from a more complex mixture. For lanthanides, contaminants are typically defined by the mineral matrix from which the metals are to be recovered and may include species like Zr, Sc, Al, Nb, Ta, Ti, Fe, Th and U [2]. For actinides, the naturally occurring species occur in the same minerals as the rare earths and hence must be separated from the above metal ions plus the lanthanides. For recovery of actinides in nuclear fuel reprocessing, the presence of fission products (and the intense radioactivity) further complicate process development and execution.

The basic outline of the elements of a process-scale separation scheme based on solvent extraction is shown schematically in FIGURE 1. Many essential features of solvent extraction-based separations are also relevant to ion exchange and membrane processes as well. The organic extractant phase is represented by the horizontal flow direction while the various aqueous streams are represented by the vertical segments. In a typical processing separation, each of the four steps (extraction, scrubbing, stripping, and solvent cleanup) is required. For analytical separations based on solvent extraction, solvent cleanup is almost never included and the process may be truncated after the extraction stage if the chemical system is favorable. In either case, the multiple contacts of the extractant with fresh (and potentially different) aqueous solutions provide many opportunities to enhance selectivity.

The two-phase and homogeneous equilibria involved in the extraction of a metal ion in a solvent extraction process are shown schematically in FIGURE 2. The energetics of each of these processes impact the position of the separation equilibrium. Metal complexation reactions (in both phases), solvation 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 accomplish the desired phase transfer and recovery. Considerable 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 factor of 100, implying 99% mutual separation of species in a single contact.

f-Element Solution Chemistry

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. Addition of valence electrons into the 4f (and 5f) valence

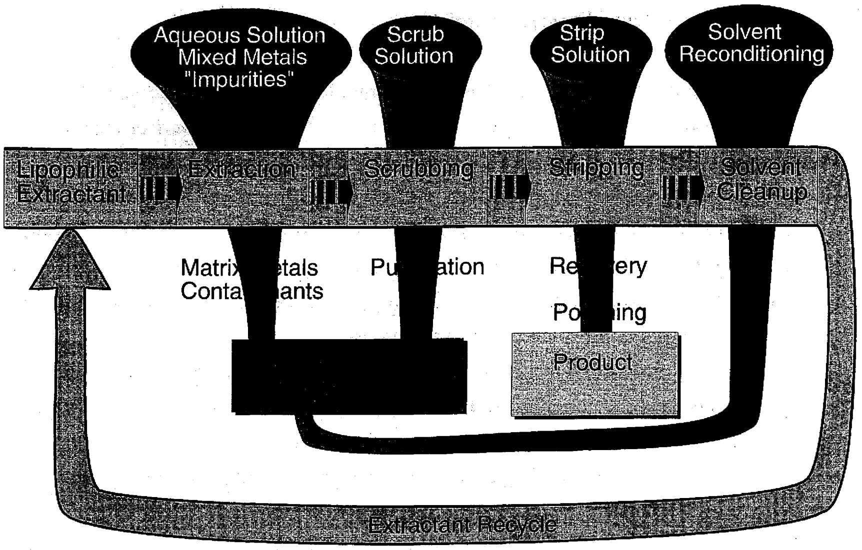

FIGURE 1. Generic flow scheme for a solvent extraction-based process.

orbitals 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 $r_{Am} \approx r_{Nd}$. 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 be used 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 respectively. Acidic conditions generally 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

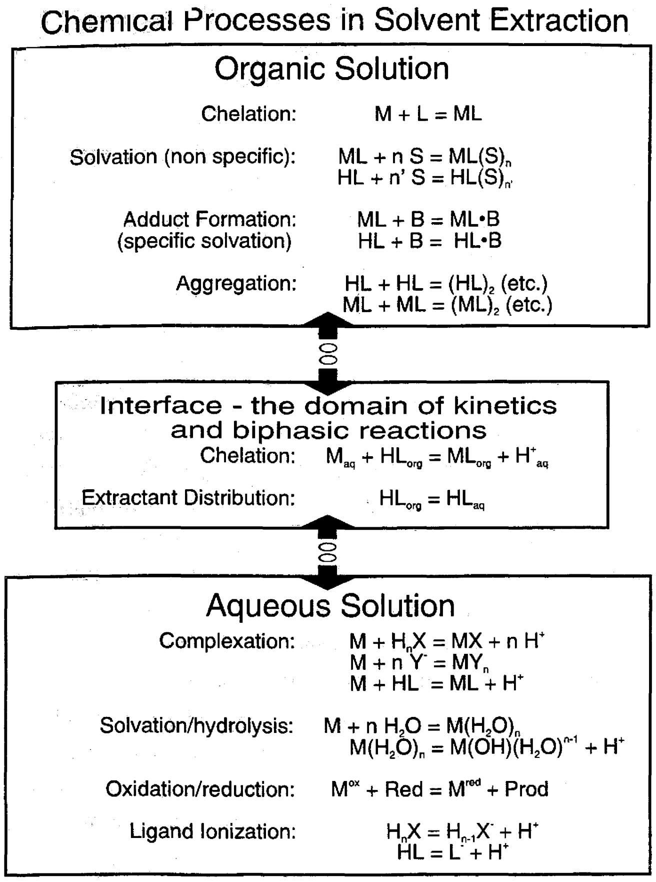

FIGURE 2. Schematic representation of pertinent equilibria in solvent extraction processes.

readily available oxidation states for these elements is of major significance in their process chemistry.

By virtue of their high charge/radius ratio, the f elements are strongly hydrated in aqueous solutions. 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/hydration 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). Ionic mobility studies indicate total ionic hydration several times higher [3]. They are also readily hydrolyzed (hydroxides precipitate at pH 1-2 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 are required. The REDOX and PUREX processes, used for hydrometallurgical processing of nuclear reactor fuels, achieve good selectivity for Pu and U through the simple expediency of oxidation state control [1]. For example, in the PUREX process, Pu(IV) and U(VI) are extracted from nitric acid. Selective stripping of Pu is accomplished by reduction to Pu(III) with Fe^{2+} or U^{4+}. Most of the U(VI) is subsequently back-extracted by reducing [HNO_3]. Solvent recycle requires washing with Na_2CO_3 that simultaneously removes TBP degradation products and residual U(VI) as the triscarbonato complex ($UO_2(CO_3)_3^{4-}$).

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 form 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 are used to accomplish 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 illustrated below.

Water Structure and Solvation in the Aqueous Phase

Choppin and coworkers [4] 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.

Solutes dissolved in water 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) reduce the structure of water thereby leading to lower net hydration energies of solutes. Small, highly charged 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, perchlorate, and thiocyanate disrupt the water structure.

Hydration of the metal ion in water is reasonably well understood. 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. Besides 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] suggest 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. 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. Ion pairing becomes 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 2, 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. Solvation of metal complexes and of polydentate chelating agents has been studied little and is generally poorly understood. We have developed information that suggests that complex and ligand solvation should not be overlooked in designing separations systems.

At elevated concentrations, cations can have an additional effect due simply to their ability to organize water structure. For example, in 10 M LiCl (density = 1.1812 g/cc, 8.47 molal solution, CRC Handbook of Chemistry and Physics, 67th edition) - a medium of importance in actinide/lanthanide separations [5], 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 8.47 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 typically 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. Similar effects can be achieved by the partial substitution of alcohol for water.

The solvent structuring effect of salts forms the basis for separation reactions based on the use of polyethylene glycols, the so-called "aqueous biphasic" systems. Polyethylene glycols have been demonstrated to partition from concentrated aqueous salt solutions. Nitrate, sulfate, carbonate, and hydroxide are particularly effective in this role, though the nature of the cation also plays a role. A key characteristic of these systems is that the immiscible phases are still largely aqueous in nature [6]. Myasoedov and coworkers have reported conditions for the separation of transplutonium elements from uranium, thorium and lanthanides [7]. In that system, the actinides partition into the polyethyleneglycol-rich phase through the action of a carrier ligand like Arsenazo III.

An additional phenomenon related to the effect of the anion on water structure is a well-known "perchlorate effect" in solvent extraction [8]. 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 perchlorate is a particularly weak ligands as compared with nitrate. An explanation for the phenomenon, and for the relative ease of extraction of metal ions from concentrated salt solutions (compared 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 [9] 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 $NaClO_4$/NaSCN, and from NaSCN solutions without supporting electrolyte (pH 4-5) exhibit strong dependence on the concentration of SCN^- (FIGURE 3). In the absence of perchlorate, the separation factors are somewhat higher at low thiocyanate concentrations, though distribution ratios are low. At constant ionic strength (5.0 M), the separation factors (S_{Eu}^{Am}) are nearly independent of $[SCN^-]$. Distribution ratios are dramatically higher in the presence of perchlorate. The free energy for extraction of both Am and Eu is 12-17 kJ/mol more favorable in the presence or perchlorate at $[SCN^-] < 1$ M.

Aqueous Complexation in Lanthanide/Actinide Separations

Perhaps the most important aspect of the aqueous medium for designing efficient metal ion separation processes is complexation. Both general purpose and cation-specific complexants can be used at any stage of a separation process to improve efficiency. Taking the PUREX process as an example, both fluoride and oxalate have been used as holdback reagents to prevent extraction of Zr^{4+} or Al^{3+} at the extraction phase. As noted above, Na_2CO_3 is used as a stripping reagent to remove traces of uranium from the PUREX solvent at the solvent cleanup stage. This minimizes the buildup of uranium in the recycled extractant solution.

The effect of aqueous complexing on separation efficiency is shown mathematically in the following discussion. If we consider the example of an acidic chelating extractant, the distribution ratio for trivalent metal ion extraction in the presence of aqueous complexing reagent is defined as:

$$D = [ML_3]_{org} /([M^{3+}] + [MX^{2+}] + [MX_2^{+}] + ...) \qquad (1),$$

assuming that the aqueous complexant does not participate in the phase transfer reaction. This expression can be rewritten in terms of the homogeneous (aqueous) phase equilibrium reaction for complex formation as:

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

The ratio $[ML_3]_{org}/[M^{3+}]_{aq}$ is the distribution ratio for the metal ion in the absence of aqueous complexes and can be expressed as $K_{ex}\,[H^+]^3/[HL]^3$, leading to the expression:

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

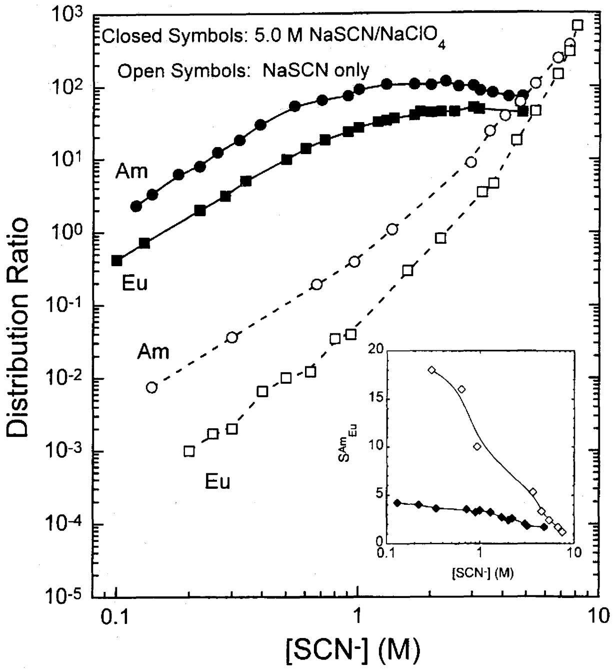

FIGURE 3. Solvent extraction separation of americium and europium using 5 % tributyl phosphate in hexane from NaSCN and 5.0 M NaSCN/NaClO$_4$ mixtures at pH 4-5 (Reference 13).

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,

$$S^{m}{}_{m'} = \frac{D^{m}}{D^{m'}} = \frac{K_{ex}{}^{m} / (1 + \Sigma(\beta_i{}^{m}[X]^{i}))}{K_{ex}{}^{m'} / (1 + \Sigma(\beta_i{}^{m'}[X]^{i}))} \qquad (4).$$

($[HL]^3/[H^+]^3$ 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 4, the most effective separations will be achieved in those systems in which the target metal ion (m in the example) 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 (dinonylnapthalene 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 when it is absent. In this system, PAA 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 $NaNO_3$. Similarly, neutral bifunctional extractants like CMPO exhibit 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+} [10].

With thiocyanate as the counter ion, americium is preferentially extracted and the separation factor S_{Eu}^{Am} is about 7 (11). As the Eu complexes are more stable than those of 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 4 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 4. 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 thioycanate ion exchange [1]. Another system useful for group separations is TALSPEAK

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

[12]. 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 5a). 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 (FIGURE 5b).

The combination of water-soluble chelating agents and cation exchange for phase separation was the basic separation method for identification of transplutonium elements [1]. Am, Cm, Bk, Cf, Es, and Fm were eluted in reverse order from Dowex 50 cation exchange resin when the eluting solution contained NH_4(citrate), NH_4-lactate, aminopolycarboxylates (like EDTA), and α-hydroxyisobutyrate. The latter reagent proved to have the best combination of kinetics and relative stability of complexes with adjacent metal ions and became the standard for this purpose.

One might guess that since the lanthanide cationic radii change so consistently across the series that there might be a number of chelating agents as effective as α-hydroxyisobutyric acid for accomplishing the isolation of individual lanthanide ions.

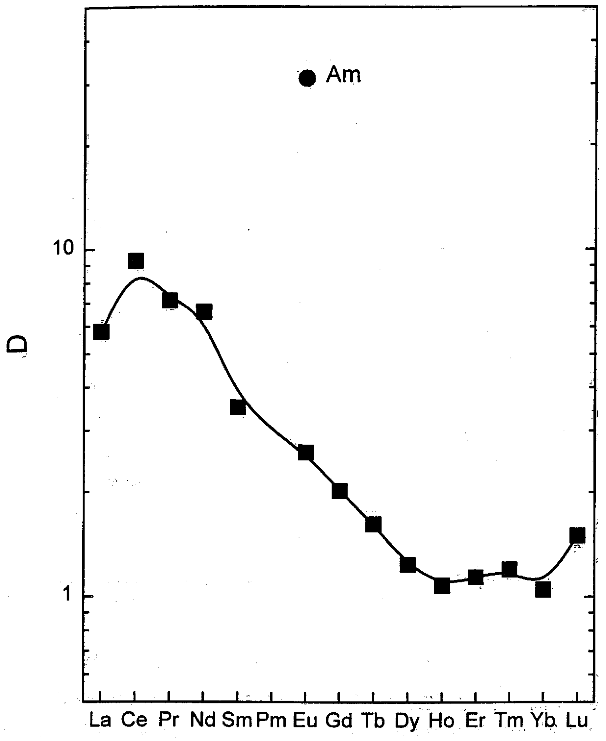

FIGURE 4. Separation of Am^{3+} (●) from the lanthanides (■) by a mixture of CMPO and TBP in Isopar L from a solution containing 0.5 M NaSCN and 0.2 M phosphonoacetic acid at pH 2.

Examination of the extensive database of critically evaluated stability constants for lanthanide complexes [13] reveals that the aqueous chemistry of the system is much more complex. There are in fact very few systems that exhibit as consistent a trend as α-hydroxyisobutyrate.

In FIGURE 6a 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

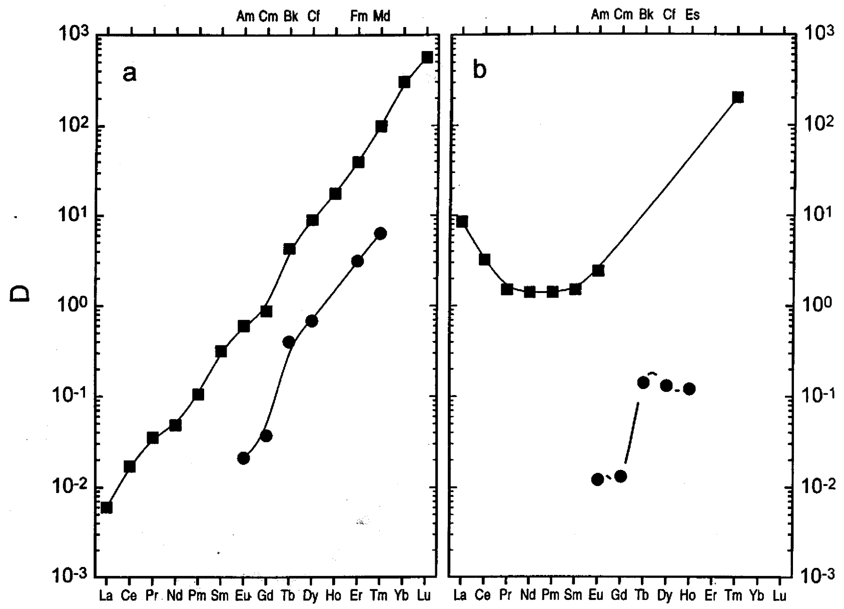

FIGURE 5. a) Distribution ratios for trivalent lanthanide (■) and actinide (●) extraction by HDEHP/toluene from aqueous nitric acid solutions, b). Distribution ratios for trivalent lanthanide and actinide cations by 0.3 M HDEHP/diisopropylbenzene from 1.0 M lactic acid/0.05 M DTPA at pH 3 (TALSPEAK).

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 radius-sensitive beyond Dy. However, thermodynamic data suggest that this selectivity is less pronounced in the corresponding 1:2 complexes [14]. The relative free energies of lanthanide aminopolycarboxylate ligands (FIGURE 6b) 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. These examples are offered as evidence that structural rigidity is a desirable feature for enhancing selectivity, but the forced ligand geometry must be compatible with the metal ion's structural or steric requirements.

Our research on the coordination complexes of f-elements with derivatives of methanediphosphonic acid [10, 15-19] has established that these complexing agents are

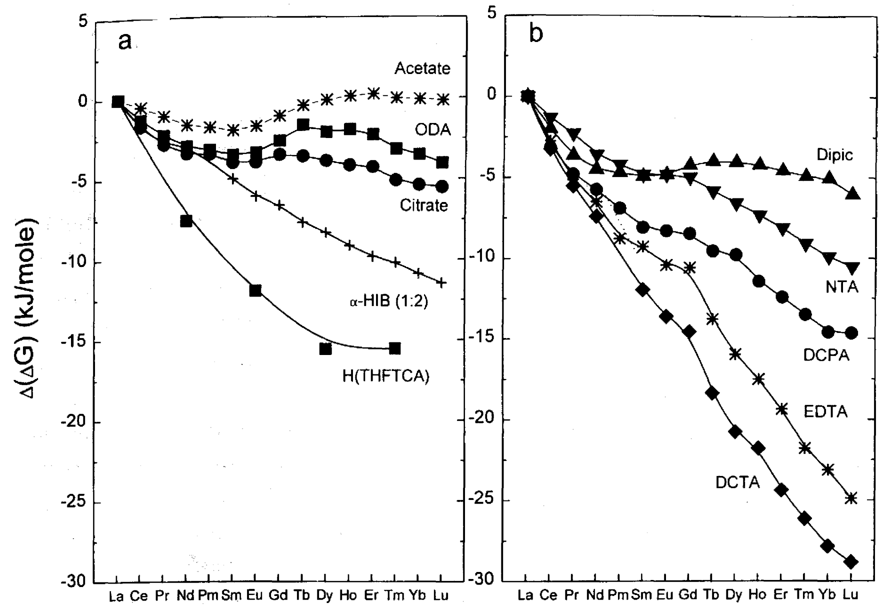

FIGURE 6. Relative free energies of lanthanide complexes (normalized to La^{3+}) with a) polycarboxylic acids (ODA - oxydiacetic acid, α-HIB - α-hydroxyisobutyric acid, H(THFTCA) - monoprotonated form of tetrahydrofuran-2,3,4,5-tetracarboxylic acid) and b) aminopolycarboxylic acids (NTA - nitrilotriacetic acid, DCPA - 2,6-dicarboxypiperidine acetic acid, EDTA - ethylenediamine-N,N,N',N'-tetraacetic acid, DCTA - trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid, dipic - 2,6-dicarboxypyridine).

very efficient general stripping agents for actinide processing. Stability constants for Eu(III) [15], Cm(III) [16], Am(III) [10], Th(IV) [17] and U(VI) [18] 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 [19]. Our research effort has also established that diphophonate complexing agents can be designed to be readily decomposed by mild treatment to facilitate waste disposal [20]. 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 [21]. 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 [22]. More recent research has led to the development of the SREX process for extraction of Sr^{2+} [23]. This solvent extraction process employs the crown ether extractant di(t-butyl cyclohexano) 18-crown-6 (di-tBuCH-18C6) 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. Because of the low specific activity of its principal isotopes ($SA(^{238}U) = 0.746$ dpm/μg, $SA(^{235}U) = 4.80$ dpm/μg), 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. Selective separation must therefore rely on the use of a reagent that can distinguish the unique geometry of the linear dioxouranyl cation.

Such a separation system has been identified [24]. The extractant solution combining CMPO for actinide extraction, diamyl(amyl) phosphonate (DA(A)P) for enhanced phase compatibility, and di-tBuCH-18C6 for Sr^{2+} extraction in Isopar L is designed for simultaneous removal of actinides and Sr 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 is shown in FIGURES 7a and 7b 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

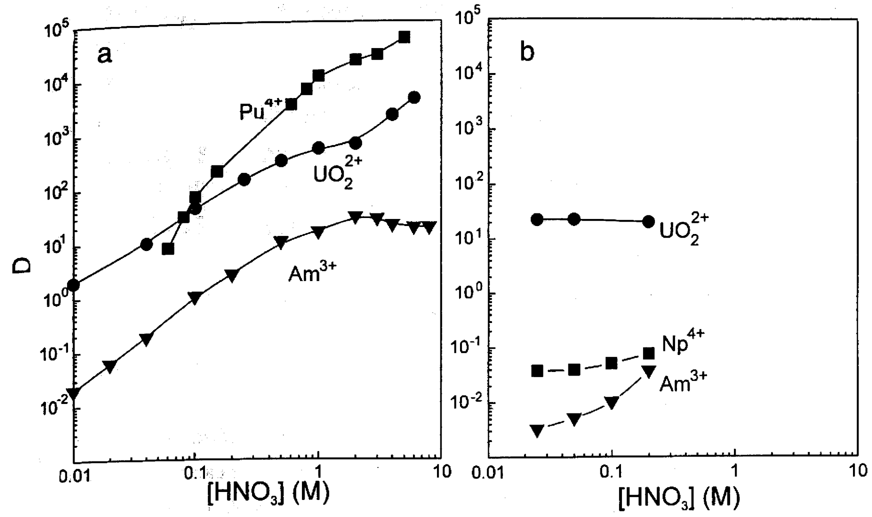

FIGURE 7 a) Extraction of trivalent, tetravalent and hexavalent actinides by TRUEX Process Solvent (0.2 M CMPO/1.2 M TBP/dodecane b) Extraction of trivalent, tetravalent and hexavalent actinides by the Combined Process Solvent (0.2 M CMPO/1.2 M DA(A)P/0.05 M di-tBuCH-18C6/Isopar L from 0.05 M $Na_2THFTCA/HNO_3$.

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.

Suggested 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.

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