On the kinetics of high temperature oxidation of copper foils:
A quantitative in situ QEXAFS investigation

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Based on previous results [1] further details of the oxidation of copper foil

\[ 2 \text{Cu} + \text{O}_2 \rightarrow 2 \text{CuO} \]

were resolved using high quality, high temperature CuO and CuO standards for Cu-K XAFS and Cu-K PCA [2] analysis. These were prepared from copper foils using the same experimental techniques as for the oxidation under study. As the reaction can be divided into a step-wise oxidation mechanism:

\[ 2 \text{Cu} + 0.5 \text{O}_2 \rightarrow \text{Cu}_2\text{O} \]
\[ \text{Cu}_2\text{O} + 0.5 \text{O}_2 \rightarrow 2 \text{CuO} \]

we attempted to check whether the formation of CuO is kinetically inhibited (delayed) or whether it takes place simultaneously to the formation of CuO. To achieve an optimal time resolution the QEXAFS technique [3] was applied. This investigation was completed by XRD and SEM investigations on samples quenched within the oxidation period.

Experiments: The investigations were performed on commercially available copper foils (GOODFELLOW, thickness: 7.8 μm, light tested, ultra pure > 99.99%) in a high temperature furnace (770 K < T < 1090 K) under continuous gas flow on beamline ROEMOII at HASYLAB. The QEXAFS experiments were carried out in transition geometry on specimens (size:7x7 mm²) fixed in a specially constructed Pt-Al₂O₃-sample. During the heating and equilibration period the conditions were established so that copper remains in the single phase field [4]. The composition of the gas mixtures thereby determines the oxygen activity. Either CO/CO₂ or Ar/H₂ gas mixtures were used. The metal oxidation was induced by fast increase of the oxygen activity to 0.21 (air) using a mass flow controller system. To guarantee reproducibility the reduction of CuO to metal after an oxidation run was also analysed followed by several oxidation-reduction runs.

Results and discussion: Between T=770 and 1090 K oxidation induced changes in the Cu-K absorption coefficient can be clearly resolved (Fig. 1). While the edge position continuously shifts to higher energies, marked by the arrow in Fig. 1, the typical absorption maxima of copper transform to a single maximum whose intensity increases with time. In addition, within the first reaction interval the pre-edge peak intensity (E=8,9835 keV) increases, but decreases as the reaction proceeds which can be related to the formation of Cu₂O, the phase intermediate formed [1] as also confirmed by PCA analysis. In SEM studies layer growth can be observed.
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Studies of the Thermodynamics of Extraction f-Elements

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Abstract

Though they were discovered in the 18th century, practical applications of individual lanthanides were not possible until the development of first ion exchange and later solvent extraction techniques. Today, solvent extraction using lipophilic organophosphorus complexants is the principal separation technique applied for lanthanide production by hydrometallurgy. Separations chemistry (coprecipitation, ion exchange, and solvent extraction) also was central to both the discovery of the individual actinides and to the preparation of samples of sufficient purity to allow elucidation of their chemical/physical properties. Solvent extraction, in the form of the PUREX process, has become the single most important separations process in actinide technology. In this report, the basic thermodynamics of extraction of actinide and lanthanide metal ions is discussed.

Keywords: thermodynamics, solvent extraction, lanthanide, actinide

Introduction

Solvent extraction separations of f elements are central to the technological development of both material science utilizing the lanthanides and to nuclear waste processing for isolation and production of actinides. For the lanthanides, acidic organophosphorus extraction reagents are most commonly used, as their extraction characteristics are suitable for both isolation of
the group from many mineral matrix cations and of individual members of the series. As the extractant in the PUREX process, tributyl phosphate (TBP) is the most important reagent in actinide processing.

The transfer of a metal ion from an acidic medium to an organic extractant solution and back is governed by the relative positions of several overlapping and competing equilibrium processes. In the aqueous phase, hydration and protonation equilibria of metal cations, chelating agents, and metal complexes, and the complexation equilibria of metal ions and ligands control the relative extractability of metal ions. In the organic phase, metal-ligand bonding, non-specific and specific solvation of complexes, and ligand-ligand interactions are the most important thermodynamic processes. Most often, solvent extraction reactions are characterized by reversible equilibria, though kinetically inert processes can contribute to apparent irreversible reactions.

In this report, the thermodynamics of extraction of lanthanide and actinide ions by different types of solvent extraction reagents will be discussed, emphasizing the general characteristics of different systems. The concept of enthalpy-entropy compensation in extraction equilibria will be examined to provide additional insights into the different separations processes.

Experimental

Most investigations of the thermodynamics of f-element solvent extraction thermodynamics have been performed relying on the change in the extraction equilibrium constant \( K_{ex} \) as a function of temperature and the Van't Hoff relationship \( \partial (\ln K_{ex})/\partial (1/T) = -\Delta H/R \). Second order thermodynamic effects from changes in \( \Delta C_P \) do not often complicate the application of this technique, as the temperature range is generally restricted by solubility and volatility considerations. There have been several reports of enthalpies measured calorimetrically in synergistic systems. In these experiments, measured enthalpies describe the addition of a co-extractant to the primary chelate complex of the extracted metal ion in a homogeneous organic phase. The experimental results described below are derived from a variety of literature reports. The reader is referred to the original references for details of the experimental procedures.

Results and Discussion

Acidic Extractants

For extraction of polyvalent metal ions by acidic extractants, the phase transfer equilibrium reaction is:

\[
K_1 \quad M^{m+}_{aq} + m \text{HL} \quad \rightleftharpoons \quad M^{m}_{L}\text{L}_m + m \text{H}^+ 
\]

where species in the organic phase are indicated by the bar above the symbol. Measured heats for metal ion extraction by this reaction include contributions from (partial or complete) dehydration of the aquo metal ion, the solvation of \( m \text{H}^+ \) ions released by the extractant, deprotonation of the extractant, degrees of freedom lost by the free ligands upon complexation, bond energies from ligand coordination of the metal ion, and readjustment of
the organic solvent from solvation of \( m \) protonated ligand species to solvation of one complex.

Perhaps the most extensively investigated reactions in f-element solvent extraction are the trivalent lanthanide-thenoyltrifluoroacetone (TTA) systems. Partly because of the consistent stoichiometry of the system (\( M:L = 1:3 \)), the \( \text{Ln}(\text{TTA})_3 \) complex is the preferred platform for studies of synergism. Dukov et al (1) report that the \( \Delta H \) for extraction of \( \text{Pr}^{3+}, \text{Gd}^{3+}, \text{and Yb}^{3+} \) from 1 M \( \text{Na/HC}1 \) is endothermic (+43.0 to +45.4 kJ/mol) and independent of the organic diluent (\( \text{C}_6\text{H}_6, \text{CHCl}_3, \text{CCl}_4 \)). Differences in the free energy of extraction between the metal ions and/or the diluents are therefore derived primarily from changes in entropy, which ranges between -43 and +24 J/mol-K. These general characteristics have been confirmed by other authors who have investigated the \( \text{Ln}-\text{TTA} \) system (2, 3). Extraction by acidic pyrazolone ligands display similar enthalpies while the extraction entropies are more positive than for TTA (4). The favorable \( \Delta S \) accounts for the generally stronger extraction of lanthanides and actinides by pyrazolones than by \( \beta \)-diketones.

Sulfonic acid extractants like dinonylnaphthalenesulfonic acid (HDNNS) are highly aggregated in organic solvents, even at very low concentrations. Micellar extractants generally exhibit little sensitivity to the size of the cation being extracted, extracting classes of metal ions (like the lanthanides) approximately equally. Otu and Westland (5) have reported that the extraction of \( \text{La}^{3+}, \text{Nd}, \text{Gd}^{3+}, \text{and Er}^{3+} \) is characterized by \( \Delta H = 7.3 \) to 10.2 kJ/mol and \( \Delta S = +69 \) to +80 J/mol-K. The narrow range of thermodynamic parameters is consistent with the low selectivity of the extraction system for individual members of the series.

Monoacidic organophosphorus extractants also aggregate in lipophilic solutions, typically existing as hydrogen bonded dimers. For some extractants, the dimer arrangement is maintained in the metal complexes, for others the ligands monomerize on complexation. Westland and Otu (6) observe that increasingly exothermic \( \Delta H \) values (-19.9 to -32.5 kJ/mol) across the series \( \text{Nd}^{3+}, \text{Gd}^{3+}, \text{Dy}^{3+}, \text{Er}^{3+} \) accounts for the increasing extraction strength by 2-ethylhexyl-p-phenylphosphonic acid (\( \text{H(EH\Phi P)} \)) in the same order.

The greater affinity of actinides for donor atoms softer than oxygen is at the heart of all successful separations of the trivalent ions of the transplutonium elements from the lanthanides (7). This difference in interaction strength has been attributed to a greater tendency for the actinides towards covalency in their bonding, which should, in principle, be manifested thermodynamically by exothermic complexation heats. Dithiophosphinic acid extractants (e.g. Cyanex 301) have been shown to exhibit separation factors of greater than 10\(^3\) for trivalent actinides ions over lanthanides of comparable size. Zhu et al (8) have reported enthalpy for the extraction of \( \text{Am}^{3+} \) and \( \text{Eu}^{3+} \) from 1.0 M \( \text{Na/HNO}_3 \) by purified Cyanex 301 as \( \Delta H_{\text{Am}} = +18.1 \) kJ/mol, \( \Delta H_{\text{Eu}} = +43.6 \) kJ/mol with corresponding entropies of \( \Delta S_{\text{Am}} = -87 \) J/mol-K, \( \Delta S_{\text{Eu}} = -66 \) J/mol-K. The enthalpy difference is the principal source of the greater selectivity of Cyanex 301 for \( \text{Am}^{3+} (\Delta(\Delta H) = -25.5 \) kJ/mol, \( \Delta(\Delta S) = +6.3 \) kJ/mol) which is consistent with increased strength of the Am-S bonding relative to that of Eu-S.

Neutral Extractants

Neutral extraction reagents accomplish phase transfer of the metal ion by solvating electroneutral complexes of the metal ions. The generic extraction equilibrium reaction is:

\[
M^{m+} + mX^- + yS \xrightarrow{K_2} MX_mS_y
\]
The most common neutral extractants for f-elements are trialkyl phosphates, phosphonates, phosphinates, and phosphine oxides. As equilibrium 2 requires the organization of \(1 + m + y\) species into one product species, one might predict that the net extraction entropy for such reactions should be consistently negative. In fact, for extraction of trivalent lanthanides, actinides, Th\(^{4+}\), and UO\(_2^{2+}\) by simple monodentate or complex bidentate organophosphorus extractants (which represent the bulk of such neutral extractant systems) the extraction entropies range between -40 and -150 J/mol-K independent of the nature of the counter ion \(Y^-\). Extraction enthalpies are exothermic and in the range of -30 kJ/mol to -90 kJ/mol.

The relative extraction of trivalent lanthanides and actinides in neutral systems has been examined comparing the relative extraction of Am\(^{3+}\) and Eu\(^{3+}\) by octyl(phenyl)carbamoyl-methylphosphine oxide (CMPO) (9), dihexyldiethylcarbamoylmethylphosphonate (DHDECMP) (10) from nitrate and thiocyanate media. The thiocyanate systems demonstrate a greater selectivity for Am equivalent to about \(\Delta(\Delta G) = 4-5\) kJ/mol (a separation factor of 5-7). Substantially more exothermic extraction enthalpies are observed in both the Eu\(^{3+}\) and Am\(^{3+}\) thiocyanate systems than in the corresponding nitrate reactions. This difference has been attributed to the energy required to transfer three SCN\(^-\) ions from the aqueous to the organic phase (9). Differences in the enthalpy of extraction of Am relative to Eu are not substantial enough to attribute the enhanced extraction of the actinide to a soft donor effect.

**Synergistic Extraction Systems**

Synergistic extraction systems combine thermodynamic features of both acidic extractants and neutral extractants according to the extraction equilibrium expression:

\[
M^{m+} + m \overline{HL} + y \overline{S} = \frac{K_3}{\overline{ML}_mS_y} + m \overline{H}^+ \quad (3)
\]

In most cases, the stoichiometry of the extracted complex with respect to the primary extractant (L) does not differ from that obtaining in the synergist-free system (equation 1). The net reaction for addition of the synergist to the extracted complex (in the organic phase) can be obtained as:

\[
\overline{ML}_m + y \overline{S} = \frac{\beta}{\overline{ML}_mS_y} \quad (4)
\]

by subtracting the appropriate equilibrium for equation 1 from equation 3. The constant \(\beta\) is \(K_3/K_1\). Because the adduct formation reaction can be formulated to occur completely in the organic phase, the heats of reaction are amenable to direct determination by titration calorimetry.

The most thoroughly investigated synergistic extraction systems involving f elements are those in which HTTA is the primary extractant. The thermochemistry of neutral organophosphorus compounds, aliphatic amines, crown ethers, bipyridyl and phenanthroline, and aliphatic sulfoxide extractants have all been investigated as synergistic reagents for lanthanide and actinide extraction by TTA. Most of the thermodynamic data were determined using the temperature variation method, some were investigated by calorimetry, and some systems have been studied using both techniques. Adduct formation reactions are generally exothermic (\(\Delta H\) between -20 and -70 kJ/mol) while the entropies cover a wide range of both
favorable and unfavorable contributions to the net equilibrium, dependent primarily on the
nature of the synergist. The tris TTA complex of the lanthanides is a di- or tri-hydrate in most
organic diluents, thus the adduct entropy partly reflects the ability of the synergist to displace
this residual hydration. Caceci et al. (11) studied using calorimetry the addition of both TBP
and triocetylphosphine oxide (TOPO) to the neutral TTA complexes of UO$_2^{2+}$, Nd$^{3+}$, and Th$^{4+}$
in benzene. The enthalpies of adduct formation were 10-20 kJ/mol more exothermic in the dry
solvent than the water-saturated equivalent. The $\Delta(\Delta S)$ values changed to almost fully
compensate for the $\Delta(\Delta H)$ and maintain $\Delta G$ constant. Crown ether adducts on the
corresponding TTA complexes (12) were characterized by entropy neutral contributions in
the trivalent lanthanide adduct, but moderately unfavorable entropies for the UO$_2^{2+}$ and Th$^{4+}$
complexes.

Addition of pyridine-based donors like bipyridyl to lanthanide TTA complexes or
dipivaloylmethane (also a $\beta$-diketone) is characterized by a strongly exothermic enthalpy (-40
to -70 kJ/mol) partially compensated by an unfavorable entropy (13-15). The synergistic
extraction of lanthanides by mixtures of TTA and trialkyl amines exhibits no temperature
dependence implying that the addition of the adduct to Ln(TTA)$_3$ is characterized by an
enthalpy of the same magnitude but opposite in sign to that of the extraction of the lanthanide
by TTA alone. This curious observation has been made for the combination of tertiary amines
and pyrazolone extractants as well.

Linear Free Energy Relationships and Enthalpy-Entropy Compensation

In equilibrium thermodynamics, changes in the enthalpy are often compensated by
entropy changes to keep the net free energy of a series of related reactions nearly constant.
Because there are so many processes contributing to metal ion solvent extraction processes,
whether enthalpy and entropy changes compensate in comparing a series of reactions is a
complex question. In Figure 1, a linear free energy plot is shown for extraction of trivalent
lanthanides, thorium, and uranium(VI) by the acidic extractants, by the neutral extractant
systems, and for adduct addition in synergistic systems as discussed above. If enthalpy-
entropy compensation is complete, the slope of the plot of $\Delta S$ vs. $\Delta H$ should be linear with a
slope equal to the average temperature of the reaction. In Figure 1a, the separate slopes for
lanthanide extraction by TTA in benzene (several authors) and by H(EHΦP) or HDNNS in
petroleum ether have slopes within one standard deviation of 298 K. For extraction of
lanthanides, Th$^{4+}$, and UO$_2^{2+}$ by neutral extractants from nitrate and thiocyanate solutions
(Figure 1b), the slope (temperature) exceeds 298 K (though it overlaps at ±2 $\sigma$) while the
process of adduct formation in synergistic extraction systems (Figure 1c) is substantially
lower than the mean experimental temperature of 298 K. If we assume that the measured $\Delta H$
values are representative of the bonding changes in the respective systems, it appears that the
neutral extractant systems are more ordered than expected, while adduct formation produces
excess entropy relative to the net bond strength increase.

These results are generally consistent with the nature of the reactions as written in
equations 1, 2, and 4. For interactions with acidic extractants, a straight-forward replacement
of water molecules by chelating extractant molecules leads to extraction, and so enthalpy-
entropy compensation is reasonable. For extraction by neutral ligands, several species must
join to form the extracted complex and the system clearly becomes substantially more
ordered. The overcompensation of $\Delta S$ (excess entropy) in adduct formation is consistent with
equation 4 if the predominant mechanism for adduct formation involves displacement of
residual waters of hydration from the extracted chelate complex. Several literature reports indicate that this is the most common mechanism for synergism.

Acknowledgment: Work performed under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract number W-31-109-ENG-38

References