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Separation of Plutonium Oxide Nanoparticles and Colloids**

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Current interest in the chemical and physical properties of nanoparticles and chemical nanostructures cannot be overstated. Significant research has been conducted on transition-metal and main-group based nanoparticles. Of interest are their properties and applications in materials synthesis, electronic devices, drug delivery and their role as either environmental contaminants or reagents for remediation.[1,2] Less exploration has occurred within nanomaterials and colloid phases of the actinide elements, the most studied of which is plutonium. In the report on this subject by Neck et al. Pu^{IV} colloids were shown to play a central role in the thermodynamic modeling of aqueous Pu speciation and redox chemistry.[3] This report built on previous knowledge that oxide/hydroxide aggregates, known as Pu polymer or colloid, significantly impact both separations and environmental chemistries.[4,5] Despite evidence to the contrary[5] Pu colloids are argued to be chemically ill defined, amorphous oxyhydroxides.[6,7] Our recent studies using X-ray diffraction and high-energy X-ray scattering (HEXS) have demonstrated that plutonium colloids may instead be oxygen-deficient, nanocrystalline PuO_2.[8] Correlating well-structured nanoclusters with plutonium colloid chemistry has important implications for understanding and controlling its solution behavior. Specifically, nanoclusters present well-defined surfaces with chemistries that can be understood, controlled and predicted.

Attempts to separate Pu colloids, the first of several reports beginning in 1956, highlighted the inability of available solvent extraction methods, designed to complex monomeric metal species, to effectively, selectively, and reversibly separate Pu colloids from other species in solution.[9–11] Previous methods used extractants that co-extract other oxidation states and metals[9,11,12] and back-extract the polymer either in a silica sol[10] or require large concentrations of salts to reverse the extraction.[9] Herein we report and demonstrate a reversible and selective separation method for Pu colloids under mild chemical conditions developed out of our solid-state and solution structural characterization of these species highlighting a well-defined surface reactivity. The results provide new insights to the chemistry of nanoparticle and colloid surfaces as well improving our understanding of Pu chemistry as it relates to environmental transport, nuclear waste handling, reprocessing and disposition.

In the structural study reported by Soderholm et al., the Pu-nanocluster $[Pu_{38}O_{56}]^{40+}$ was surface-decorated by capping water molecules and chloride ions to yield the formula $[Pu_{38}O_{56}Cl_{54}(H_2O)_8]^{14-}$.[8] Dissolution of the clusters in an aqueous solution of LiCl produces a green solution with an optical spectrum identical to that which serves as the operational definition of Pu polymer.[13] Analysis of HEXS from a solution of dissolved crystals of Pu nanoclusters has shown the cluster unit to remain intact.[8] Addition of 6 M HCl to this solution causes an immediate color change from green to red, the original color of the crystals, resulting in the optical spectrum in Figure 1. The spectrum obtained does not correspond to any previously known aqueous plutonium chloride species.[12,14] The color change is reversible upon dilution with water and when the acidified red solution is allowed to evaporate, red crystals suitable for X-ray diffraction are obtained. The crystals have the same $[Pu_{38}O_{56}]^{40+}$ core as those previously reported[8] but only 42 Cl^- decorate the surface, leaving the $[Pu_{38}O_{56}Cl_{42}(H_2O)_{20}]$ cluster with a 2− charge. The structure of this cluster is shown in Figure 2 and additional information is provided in the Supporting Information.[15]

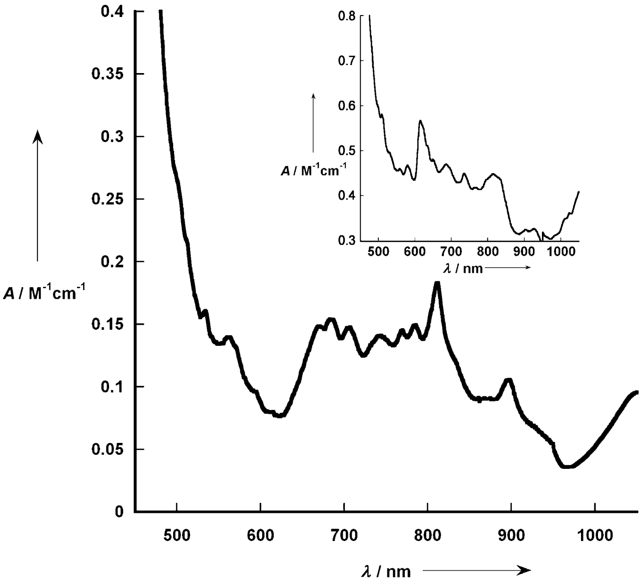

Figure 1. The optical spectrum of the red solutions obtained by dissolving Pu_{38} crystals in 2 M LiCl acidified with 6 M HCl is contrasted with that obtained from a green solution of the Pu_{38} crystals dissolved in 2 M LiCl (inset). The inset spectrum corresponds to that of Pu colloid.

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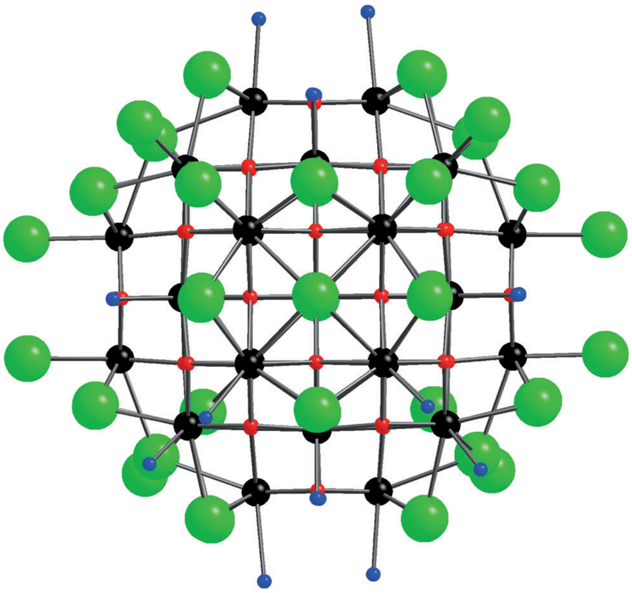

Figure 2. Crystal structure of $Li_2[Pu_{38}O_{56}Cl_{42}(H_2O)_{20}]\cdot 15\,H_2O$. The surface water molecules are shown as blue spheres, the chloride ions are in green. The plutonium and oxygen in the oxide core are rendered black and red, respectively.

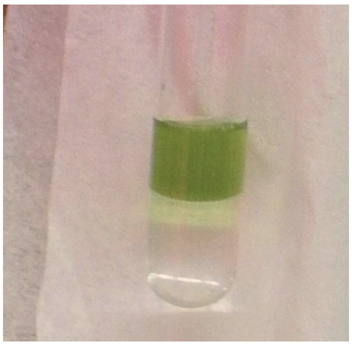

Figure 3. Demonstration of the partitioning of the green colloidal plutonium from the aqueous phase,bottom, to the lighter organic TCA/*n*-octanol phase, top.

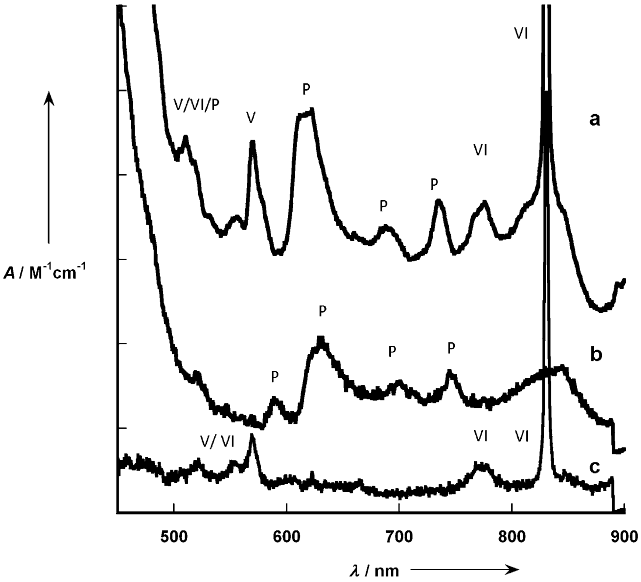

Figure 4. a) UV/Vis spectrum of the original aqueous phase containing Pu colloids (P) with $Pu^{V}O_2^{+}$ (V) and $Pu^{VI}O_2^{2+}$ (VI); b) the separated organic phase containing only Pu colloids; c) the remaining aqueous phase containing $Pu^{V}O_2^{+}$ and $Pu^{VI}O_2^{2+}$. The polymer peaks are slightly red-shifted upon extraction into octanol.

The rapid interchange of the optical spectra suggests a surface reaction involving ion- or ligand-exchange reaction between water and chloride that leaves the oxide core structurally unperturbed. Surface-ion lability is supported by the different number of H_2O/Cl^- in the structure presented in Figure 2 and the previous report.[8]

Ligand lability on a well-defined nanocluster surface suggests a potentially new separations scheme exploiting this reactivity. The dative interaction between carboxylic acids and metal oxide surfaces is well documented in the literature. Nanoparticle surfaces have been shown to adsorb carboxylic acids and other surfactants; such functionalization has been exploited to control particle growth and physical properties of the nanoparticles and other actinide oxide clusters.[1,16] Inspired by this chemistry we chose trichloroacetic acid (TCA) as a prototypic extractant because of its solubility in alcohols and chose *n*-octanol because of its immiscibility with water.

Shown in Figure 3 is the partitioning of the aged colloidal Pu[13] phase into the *n*-octanol layer from the aqueous phase using 1 M TCA in octanol. UV/Vis spectra of these phases are presented in Figure 4. The top trace in Figure 4 is from the original aqueous phase containing the aged plutonium colloid along with ions of $Pu^{V}O_2^{+}$ and $Pu^{VI}O_2^{2+}$ prior to contact with TCA/*n*-octanol. The coexistence of the colloid with other oxidation states of Pu is expected and underscores the central role of the colloid in Pu speciation.[3,6,12,17] The middle trace in Figure 4 shows the spectrum for the extracted organic phase and contains only the features expected for Pu colloid with no indication of other species. An optical spectrum of $[Pu_{38}O_{56}Cl_x(H_2O)_y]^{40-x}$ extracted under the same conditions is presented in the Supporting Information.

Note that the Pu colloid is selectively extracted into the organic phase leaving the other plutonium species in the aqueous phase (Figure 4, bottom trace). Such selectivity is unprecedented in the known extraction chemistry of Pu colloids.[9–12]

HEXS data were collected to verify that the colloids remained intact in the organic phase (Figure 5 a). HEXS provides atomic-pair correlations and is sensitive to metal–metal correlations encountered in nanoparticles and colloids.[18] The most intense peaks observed in the HEXS data arise from the Pu–Pu correlations in the PuO_2 framework upon which the colloids are based. The precipitous fall-off of the peak intensity envelope at longer distances is indicative of the oxide particles' finite size. Transference of the signature X-ray scattering envelope from the aqueous phase to the organic phase demonstrates that the particle core remains intact upon extraction. Moreover, it is only the Pu colloids being extracted and not the mononuclear Pu species traditionally targeted for liquid–liquid separations schemes. FT-IR

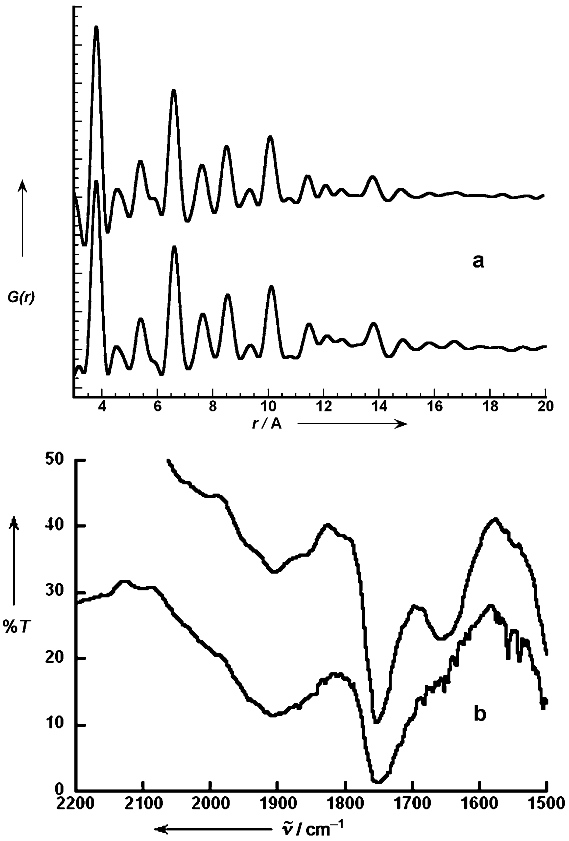

Figure 5. a) Atomic pair-correlation functions obtained from HEXS data showing the conservation of the oxide particle core upon extraction from the aqueous (bottom) to the organic phase (top). The large peaks in the pair-correlation functions are Pu–Pu correlations, indicative of small PuO_2-based particles. b) FTIR spectra of the TCA/*n*-octanol phase before extraction (bottom) and after extraction of Pu colloids (top). The new peak after extraction at 1658 cm^{-1} is consistent with a carboxylic acid coordinated to the particle surface.

data collected on the *n*-octanol/TCA phase before and after extraction of the Pu colloids (Figure 5b) shows an absorption at 1753 cm^{-1} belonging to the carbonyl stretching frequency of TCA, and a new peak at 1658 cm^{-1} after extraction consistent with the coordination of the TCA to the colloid, in agreement with studies demonstrating dative interactions between the carbonyl of carboxylic acids and Lewis acid sites on metal oxide surfaces.[19] Similar features are observed in the extraction of other tetravalent metal dioxides, as demonstrated by results on CeO_2 particles presented in the Supporting Information.

These results show that the chemical properties of the particles are changing because of reactions occurring at their surfaces. Attempts to crystallize the surface-modified cluster with TCA or other carboxylic acids have been unsuccessful to date.

Measurement of the distribution ratios, $D_{Pu} = [Pu_{org}]/[Pu_{aq}]$, provides additional insight into the mechanism and properties of the separation. A series of D_{Pu} measurements were made varying the concentration of TCA (0 to 5 M), aqueous-phase electrolyte ($NaNO_3$, NH_4Cl, NH_4ClO_4, $(NH_4)_2SO_4$), and pH of the aqueous phase (HCl, HNO_3, $HClO_4$). The results are summarized here and the data are available in the Supporting Information. For an aqueous phase containing Pu colloids (1 mM Pu_{tot}) in 1 M $NaNO_3$ and 0.04 M HNO_3, the D_{Pu} reached a maximum value of ca. 10 when the organic phase contained at least 1 M TCA. Below this concentration of TCA the extraction was less effective with no partitioning of Pu to the organic phase in the absence of TCA. Similar results were obtained in ClO_4^- and Cl^- media.

Under high anion concentrations, > 5 M Cl^- or NO_3^-, small decreases in the D_{Pu} were observed. In the case of perchlorate, no decrease in the extraction efficacy is observed consistent with the weakly coordinating nature of perchlorate. Conversely, only small concentrations of SO_4^{2-} (0.25 M) relative to the TCA concentration (5 M) are required to completely inhibit the separation of the Pu particles. These results agree with known empirical trends in coordination chemistry.[20] We ascribe these observations to a competition between the TCA and the anions for the surface of the particles.

The reactions observed between TCA and the Pu colloids should be reversible or inhibited by protonation of the TCA through acid addition to the aqueous phase. In the presence of > 2 M HNO_3 inhibition of the extraction is observed due to either protonation of the TCA or NO_3^- competition with the TCA for surface coordination. Extraction in the presence of $HClO_4$, the most weakly coordinating of the anions studied, tests the acid–base properties while minimizing the ligand-exchange competition at the surface. No inhibition or reversibility is observed as high as 5 M $HClO_4$ suggesting that the colloid surfaces are less sensitive to acid–base reactions than the ligand-exchange reactions.

The insensitivity of Pu colloids to acid–base reactions has been observed before.[13,21] The efficacy of the extraction at very high acidities in the absence of a coordinating anion may indicate that the colloid surface sites are strongly ionizing, thus able to deprotonate and bind the TCA well below its equilibrium pK_a value of 0.77. However, the FT-IR data show that the interaction may also be consistent with association of the carbonyl oxygen of the protonated TCA with a Pu Lewis acid site on the colloid surface. Notwithstanding the irreversibility of the TCA–colloid interaction by adjustment of the acidity, the extraction of the colloid is reversed by sulfate anions. Colloids initially extracted from a nitrate-containing solution can be reversibly stripped from the organic to the aqueous phase using $(NH_4)_2SO_4$. The reversibility of the extraction reinforces the hypothesis that the surfaces of plutonium colloids are reactive towards ligand exchange reactions. Methods aimed at quantifying the surface–ligand interactions in this system are currently being explored.

The previous study suggesting that Pu colloids may have a structurally well-defined surface[8] lead to a new approach to its isolation, thus providing the basis to build a separations scheme. We demonstrated that the surfaces of Pu colloids present chemistry that can be manipulated, understood, and predicted. Despite the reactivity towards ligand and ion-exchange reactions, the surface appears inert towards protonation and deprotonation reactions. The application of these observations to a novel separations scheme lies in the ability to target colloids or nanoparticles of metal oxides directly rather than the mononuclear metal species that must first be generated under harsh chemical conditions. These results also demonstrate the exceptional complexity surrounding the surface chemistry of these particles and pose significant questions regarding our understanding and prediction of plutonium reactivity and transport in subsurface geological environments.

Experimental Section

Distribution ratio measurements. Aged colloid solutions of ^{242}Pu were prepared using methods available in the literature resulting in a Pu colloid stock solution $[\mathrm{Pu}]_{\mathrm{tot}} = 15$ mM in 0.04 M HNO_3.[13] For the solvent extraction experiments, solutions of 1 mM Pu (0.5 mL) in the desired electrolyte were contacted with an equal volume of TCA/*n*-octanol at the desired concentrations of TCA. The phases were vortexed for 1 min, and centrifuged to achieve phase separation. The *n*-octanol solutions were pre-equilibrated with water prior to use. Pu concentrations and distribution ratios were determined using liquid scintillation counting. Additional details are available in the Supporting Information.

Synthesis of $Li_2[Pu_{38}O_{56}Cl_{42}(H_2O)_{20}](H_2O)_{15}$: The plutonium oxide cluster presented here was isolated upon recrystallization of $Li_{12}[Pu_{38}O_{56}Cl_{54}(H_2O)_8](H_2O)_x$, from an equivolume mixture of 6 M HCl 2 M LiCl solution. The $Li_{12}[Pu_{38}O_{56}Cl_{54}(H_2O)_8](H_2O)_x$ starting material was produced by an alternate method to the previously reported synthesis.[8] A solution of Pu^{IV} (2 mL, 50 mM) in concentrated HCl is brought to a boil. A total of 2 mL of saturated LiOH (ca. 2 M) is added dropwise in small additions while the solution is boiling. The solution is continued to boil, reducing the volume by half and cooled. Crystals appear from the solution near complete evaporation within weeks. The crystals are often associated with a pale orange gel or viscous red solution. Crystallization is not quantitative and a more direct synthetic route is being investigated.

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[15] Crystal data: $Li_2[Pu_{38}O_{56}Cl_{42}(H_2O)_{20}](H_2O)_{15}$, $M_r = 12140.9$, crystal size $= 0.10 \times 0.08 \times 0.05$ mm, cubic, $Ia\bar{3}$, $a = b = c = 35.315(6)$ Å, $\alpha = \beta = \gamma = 90.00°$, $Z = 8$, $\rho_{\mathrm{calcd}} = 3.662$, $\mu = 11.752\ \mathrm{mm}^{-1}$, $\mathrm{Mo}_{K\alpha}$ 0.71073 Å, $T = 100$ K, $2\Theta_{\max} = 56.54°$, measured reflections 282018, independent reflections 9123, $R_{\mathrm{int}} = 0.0685$, $R1 = 0.0391$, $wR2 = 0.1248$ ($I > 2\sigma I$), GOOF = 1.099, residual density (max/min) 5.611/−2.309. Data were collected on a Bruker APEX II diffractometer. Absorption corrections were applied using the program SADABS. The structure solution was solved using direct methods and subsequent full-matrix least-squares refinements on F^2.[22] Attempts to identify the Li^+ cations were unsuccessful and are not included in the model. Refinements modeling the residual electron density outside the cluster as water molecules did not improve the model. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-423422.

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