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Experimental Measurements of U24Py Nanocluster Behavior in Aqueous Solution

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Summary

Uranyl peroxide nanoclusters may impact the mobility and partitioning of uranium at contaminated sites and could be used in the isolation of uranium during the reprocessing of nuclear waste. Their behavior in aqueous systems must be better understood to predict the environmental fate of uranyl peroxide nanoclusters and for their use in engineered systems. The aqueous stability of only one uranyl peroxide nanocluster, U60 ($K_{16}Li_{44}[UO_2(O_2)OH]_{60}$), has been studied to date[1]. In this study, we measured the aqueous stability of a second uranyl peroxide nanocluster, U24Py ($Na_{30}[(UO_2)_{24}(O_2)_{24}(HP_2O_7)_6(H_2P_2O_7)_6]$), in batch systems as a function of time, pH, and nanocluster concentration, and then compared the aqueous behavior of U24Py to U60 to determine whether the size and morphology differences result in differences in their aqueous behaviors. Systems containing U24Py nanoclusters took over 30 days to achieve steady-state concentrations of monomeric U, Na, and P, illustrating slower reaction kinetics than parallel U60 systems. Furthermore, U24Py exhibited lower stability in solution than U60, with an average of 72% of the total mass in each nanocluster suspension being associated with the U24Py nanocluster, whereas 97% was associated with the U60 nanocluster in parallel experiments [1]. The measurements from the batch experiments were used to calculate ion activity product (I.A.P.) values for the reaction between the U24Py nanocluster and its constituent monomeric aqueous species. The I.A.P. values, calculated assuming the activity of the U24Py nanocluster is equal to its concentration in solution, exhibit a significantly lower nanocluster concentration dependence than those I.A.P values calculated assuming an activity of one for the nanocluster. The inclusion of a deprotonation reaction for U24Py minimizes the pH dependence of the calculated I.A.P. values. The modeling results suggest that the U24Py nanocluster experiences sequential deprotonation. Taken together, the results indicate that the aqueous behavior of the U24Py nanocluster, like that of U60, is best described as that of an aqueous complex.

Keywords: Nuclear fuel cycle, Uranyl peroxide nanocluster, Aqueous stability, U24Py, U60

1. Introduction

Uranyl peroxide nanoclusters represent a class of radionuclide-bearing compounds that could be present in the environment and may play a role in future radionuclide separation processes. These nanoclusters could potentially form at contaminated sites such as at Savannah River, Hanford, and Fukushima [2-3]. Additionally, uranyl peroxide nanoclusters may be used in an advanced nuclear fuel cycle, as a means of isolating and recycling uranium from nuclear waste [4-6]. To predict the environmental fate of uranyl peroxide nanoclusters or for their use in engineered systems, their behavior in aqueous systems must be better understood.

Uranyl peroxide nanoclusters are a unique class of uranium materials that rapidly self-assemble in aqueous solution and are similar in topology to some transition metal polyoxometalates [4, 7, 8, 9, 10, 11]. The nanoclusters can exist in a crystalline phase composed of an assemblage of nanoclusters, and as isolated or aggregated nanoclusters in aqueous solution [1]. In under-saturated solutions, crystals of uranyl peroxide nanoclusters dissolve rapidly to liberate isolated or aggregated nanoclusters into solution [12]. They have been shown to be at least metastable in solution, with some persisting for months [2]. Isolated uranyl peroxide nanoclusters in aqueous solution can be separated from aqueous monomeric species by ultrafiltration [6]. Flynn et al. [1] examined the aqueous behavior of one type of isolated uranyl peroxide nanocluster in solution (U60, $K_{16}Li_{26}[UO_2(O_2)OH]_{60}$). In their study, the relationship between the isolated U60 nanoclusters in solution and simpler uranyl species was found to be best represented as a dissociation reaction. The calculated ion activity product (I.A.P.) values for U60 showed the least variation as a function of pH and U60 concentration when U60 was treated as an aqueous complex with an activity equal to its concentration in solution. It remains unclear whether the behaviors of all uranyl peroxide nanoclusters in aqueous solution are controlled by their size, chemical composition, molecular charge in solution, or a combination of these and possibly other factors.

To further understand the behavior of isolated uranyl peroxide nanoclusters in aqueous solution, this study examines the uranyl peroxide nanocluster U24Py, $Na_{30}[(UO_2)_{24}(O_2)_{24}(HP_2O_7)_6(H_2P_2O_7)_6]$. U24Py consists of 24 uranyl peroxide hexagonal bipyramids that are arranged into six square units in which the uranyl ions are linked by peroxide bridges. These six square units are linked through pyrophosphate bridges to form an oblate cage cluster with dimensions of 1.70 nm x 1.89 nm x 1.99 nm [13]. The U24Py nanocluster differs in composition, shape, and size to U60 nanoclusters. U60 is composed of 60 uranyl peroxide bipyramids, linked by peroxide and hydroxide bridges to form pentagonal and hexagonal units that are arranged into a spherical cage with a diameter of 2.4 nm in its crystalline form [7]. The size of the U24Py and U60 nanoclusters raises a primary question that our research addresses, whether compounds of this size behave more like bulk solid phases or like large aqueous complexes. The solubilities of micron-sized particles or larger are independent of particle size; however, the solubility of smaller particles may increase dramatically with decreasing particle size. With decreasing particle size, nanoparticle properties, including solubility, are thought become increasingly dominated by surface free energy effects [14]. According to the Ostwald-Freudlich equation, particle solubility increases with decreasing particle size for particles less than approximately 20 nm [15-17]. Flynn et al. [1] demonstrated that the boundary between aqueous species and solid phases is not a sharp one, and nanoscale materials can exhibit distinct

aqueous behaviors from either smaller monomeric aqueous species or bulk solid phases. With relatively few experimental studies on the aqueous behavior of nanoclusters and nanoparticles in the sub 10 nm range, our objective was to compare the interactions of U24Py and U60 with aqueous solutions in order to further our understanding of this transitional behavior.

We investigated whether the size and morphology differences between U24Py and U60 lead to differences in their behavior in aqueous solution by measuring the distribution of mass between U24Py nanoclusters in solution and their constituent monomeric aqueous species as a function of time, pH, and initial nanocluster concentration. The measured pH and monomeric U, P, and Na concentrations were used to calculate the I.A.P values for each experiment, accounting for aqueous speciation of each element in solution. We used the I.A.P. values to test whether the nanocluster activity in solution affects the calculated I.A.P. value, as would be expected for an aqueous complex, or if the I.A.P. is independent of the nanocluster activity, analogous to how a macroscopic solid phase would equilibrate with an aqueous phase. Together with the corresponding study of U60 [1], this study furthers our understanding of the behavior of uranyl peroxide nanoclusters in aqueous solution and enhances our ability to predict how these macromolecules would affect uranium distribution and mobility in environmental and engineered systems.

2. Methods and Materials

2.1. Synthesis and Characterization of Nanoclusters

U24Py crystals were synthesized using a method adapted from Ling et al. [13]. A solution was prepared by adding 0.5 mL of 0.5 M uranyl nitrate, 0.5 mL of 30% hydrogen peroxide, and 0.5 mL of 40% tetraethylammonium hydroxide to a 20 mL uncapped glass vial. After the heat of the reaction dissipated and outgassing stopped, 1.5 mL of 0.1 M sodium pyrophosphate decahydrate and 1.5 mL of 0.5 M iodic acid were added to the vial. After 14 days, the U24Py crystals were harvested under vacuum filtration on a Whatman cellulose membrane with an 11μm pore size once they reached 2-10 mm. During harvesting the crystals were rinsed with approximately 5 mL of 18 MΩ ultrapure water and allowed to dry under vacuum.

The purity of samples of the harvested U24Py crystals was tested using a Bruker APEX X-ray diffractometer with a Mo *K*α radiation source. A single crystal was rinsed before being placed in Infinium oil, and cooled to 110 K for data collection. A complete sphere of data was collected using four sets of exposures with frame widths of 0.3° in ω for each crystal. The program APEX II was used to correct for polarization and background effects [18], and the program SHELXTL was used to determine structural solutions [19].

2.3. Electrospray Mass Spectrometry

The presence of isolated U24Py nanoclusters within the solutions was verified using qualitative electrospray ionization mass spectrometry (ESI-MS) at each sampling point. The ESI-MS spectra were recorded in negative-ion mode with a Bruker micrOTOF-Q II high resolution quadrapole time of flight mass spectrometer apparatus at the following settings: 3600 V capillary voltage, 0.4 bar nebulizer gas, 4 L/min dry gas, and 180°C dry gas temperature. The samples were introduced through direct infusion at 10 μL/min and scanned over 50-10,000 M/Z with the

data averaged over 2-5 minutes. Data was deconvoluted using either standard Bruker large molecule/protein algorithms or licensed MaxEnt software. Two broad peaks centered at M/Z values of 1460 and 1600 were determined to be signatures of U24Py. The presence of multiple peaks is attributed to the creation of multiple charge states of U24Py during ionization due to the subtraction of differing amounts of Na ions from the U24Py nanocluster. Broad peaks are commonly observed when large clusters travel through an ionizing field, which strips cations from the cluster, producing daughters with a similar charge but slightly different masses.

2.2. Aqueous Partitioning Experiments

Using a similar method to that reported by Flynn et al. [1], 16 batch partitioning experiments were conducted at room temperature and pressure (25° C and 1 atm) in an anaerobic glove box with an atmospheric composition of 95% N_2 and 5% H_2 in order to eliminate atmospheric CO_2 and the presence of aqueous uranyl carbonate complexes. U24Py suspensions were prepared in Teflon reaction vessels by dissolving a known mass of U24Py crystals into 18MΩ ultrapure water, which had been bubbled with 95% N_2 and 5% H_2 for 30 minutes. The complete dissolution of the U24Py crystals was verified in control experiments, in which the total U concentration did not vary between samples taken from suspensions before and after passing through a 0.2 μm PTFE membrane (Table S1). Suspensions of U24Py were prepared at three nanocluster concentrations of approximately 0.9, 1.8, and 2.8 g/L. Suspensions were adjusted using 1 M LiOH to achieve and maintain pHs of 8.50 ± 0.15, 9.00 ± 0.02, or 9.50 ± 0.01. Each nanocluster concentration and pH experiment was performed at least in duplicate, with the exception of the pH 9.5, 0.9 g/L and the pH 9.5, 1.8 g/L experiments. A complete table of experimental conditions is shown in Table S2 in the Supplemental Information. The initial solutions did not contain monomeric U, P, or Na; therefore, all subsequent measurements of aqueous monomeric U, P, and Na indicate the dissociation of the U24Py nanoclusters. In the experimental systems, steady state was only approached from under-saturation with respect to the U24Py nanoclusters, as a pure yield of U24Py has only been synthesized from polydisperse solutions.

The sealed reaction vessels were rotated at 40 rpm within an anaerobic glove box and allowed to equilibrate for 24 hours before the first sampling. Sampling was performed, approximately every 7 day over 47-48 days, within an anaerobic glove box to insure that neither the experimental systems nor the samples were exposed to atmospheric O_2 or CO_2. During sampling, the pH of each experimental system was measured inside the glove box using a Thermo-Orion Model 420 pH probe with a Thermo-Orion semi-micro glass combo electrode. The volume of base added and sample removed during sampling was tracked throughout the duration of the experiments and used to calculate the Li concentration and the ionic strength of each system at each sampling point. The sample aliquot from each experiment was passed through a 0.2 μm PTFE membrane to remove any micron-sized precipitates while allowing the passage of the isolated U24Py nanoclusters as well as monomeric aqueous species. The sample was subsequently divided into two portions. The first is referred to as ‘before molecular weight filtration’ (BMWF). The second portion, designated ‘after molecular weight filtration’ (AMWF), was passed through a 3,000 Da molecular weight sieve, which allowed the passage of monomeric aqueous species but removed the isolated U24Py nanoclusters (which are 10,051 Da as isolated nanoclusters in solution, as calculated from the nanocluster stoichiometry)(a

schematic of the filtration process is shown in Fig.1) The ability of the molecular weight filtration to completely separate the U24Py nanoclusters from solution was verified through control experiments using ESI-MS to detect clusters in solution.

The BMWF ESI-MS spectrum contained the two characteristic peaks of the U24Py nanoclusters; these peaks are absent in the AMWF spectrum, as shown in Fig.2. Therefore, the elemental composition of the BMWF sample represents the total concentration of each of the elements in solution, including both the elements present in the U24Py nanoclusters and those present as monomeric aqueous species. The AMWF elemental composition represents only the concentration of the monomeric aqueous species that are from the dissolution or dissociation of the U24Py nanoclusters. The difference between the BMWF and AMWF elemental concentrations was used to determine the concentration and elemental composition of the U24Py nanoclusters in solution. Samples collected for U, P, and Na analysis were diluted and acidified before analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES) (A detailed description of the ICP-OES methods can be found in the Supplemental Information.

3. Results and Discussion

3.1. Batch Experiments

The measured BMWF concentrations of U, P, and Na did not exhibit a consistent change as a function of time for the duration of the experiments, as shown by a representative experiment in Fig. 3A (the complete data set is shown in Figs. S2, S3, and S4 in the Supplemental Information). The lack of significant variation in the BMWF concentrations as a function of time indicated that the U24Py crystals rapidly and completely dissolve with no micron-scale secondary precipitates forming in solution over the duration of the experiments.

The AMWF U, P, and Na concentrations slowly increased for the first 28 days of the experiment and stabilized by Day 34. The AMWF concentrations showed little consistent change from Day 34 through the termination of the experiments. This indicates that each of the experimental systems reached a steady-state (Figs. 3B, S5, S6, and S7). The presence of monomeric U, P, and Na in the AMWF samples indicates unambiguously that the isolated U24Py nanoclusters dissociate to some extent in solution. The observed perturbations in the AMWF concentrations after steady-state was achieved were likely due to a combination of analytical and experimental uncertainties, such as small pH fluctuations between samples and error associated with the large dilutions required for ICP-OES analyses. Over the course of the experiment, 21 – 36% of the mass of the nanoclusters was transformed into monomeric aqueous species. The presence of the two peaks attributed to U24Py throughout the duration of the experiments in the ESI-MS spectra indicates that the nanoclusters did not completely dissociate over the sampling period (a representative ESI-MS spectrum from Day 47 is shown in Fig. S1 of the Supplemental Information).

For each experiment, we used the average concentration of the final three sample points, (from Days 34-48) to represent the AMWF concentration of each element measured at steady-state under each experimental condition. The measured AMWF U, P, and Na concentrations exhibited no significant trend as a function of either pH or nanocluster concentration (Figs. 4 and

5). The AMWF P/U and Na/U molar ratios averaged over all of the experiments were 4.01 ± 0.77 and 7.07 ± 1.45, respectively (Fig. 6). These molar ratios showed significant higher concentrations of monomeric P and Na in solution when compared to the expected P/U and Na/U molar ratios of 1.00 and 1.25, respectively based on the crystalline stoichiometry. Additionally, the Na/P ratio in the isolated nanocluster, calculated from the difference between the BMWF and AMWF Na and P concentrations, was 1.26 ± 0.32 and approximately equals the 1.25 Na/P ratio of crystalline U24Py [13]. The higher AMWF concentrations of P and Na relative to the U concentration and the nanocluster ratio of Na/P being consistent with the crystalline stoichiometry is indicative of one of two scenarios: 1. P and Na were leached congruently from the intact nanoclusters, or 2. a secondary submicron-scale U phase that is able to pass through a 0.2 μm filter membrane and consists of negligible amounts of P or Na precipitated in the experimental solutions and. As P is present in the nanocluster as pyrophosphate, the loss of P from the nanocluster would result in the loss of the pyrophosphate bridges from the nanocluster structure. This loss, in turn, would leave uranyl bipyramids with fewer than their full complement of pyrophosphate bridges; it is unlikely that the nanocluster would remain intact lacking these integral uranyl pyrophosphate bridges. Hence, with the calculated Na/P ratios in the isolated nanoclusters being consistent with the stoichiometric dissolution of the U24Py nanoclusters, the observed deficit of U in the AMWF solutions is most likely due to precipitation of a submicron uranyl phase that is free of P and Na.

3.2. Metaschoepite Solubility Calculations

Thermodynamic modeling was used to determine whether a secondary uranyl phase could be buffering the aqueous U concentrations, thereby explaining the observed deficit of U in the AMWF calculated P/U and Na/U molar ratios. The most likely known mineral phase that could be present at the experimental pH values would be the uranyl hydroxide mineral metaschoepite [$UO_3(H_2O)$]. To test whether a metaschoepite phase would be expected to precipitate under the experimental conditions, the solubility of metaschoepite was calculated for the experimental conditions. The dissolution/precipitation reaction for metaschoepite can be expressed as:

$$H^+ + UO_3(H_2O) \leftrightarrow UO_2^{2+} + 2{*}H_2O \quad (1)$$

with the solubility product, Ksp, represented as:

$$\mathrm{Ksp} = a_{UO_2^{+2}} \cdot a_{H^+} \quad (2)$$

where *a* represents the thermodynamic activity of the subscripted species, and the activities of water and the metaschoepite are taken to be equal to one.

The Ksp value used for these calculations was reported by Gorman-Lewis et al. [20]. Activity coefficients for the aqueous ions were calculated using the extended Debye-Hückel equation with the following constants: A = 0.5085, B = 0.3281, å = 5.22, and b = 0.02 [21].

$RbNO_3$ was chosen as the most reasonable species for approximating the values of å and b based on cation size, as these values have yet to be determined for a uranyl-dominated system. For the purpose of calculating the expected metaschoepite solubility under the experimental conditions, the ionic strength was estimated as 0.0069 M. The standard-states used for solid phases and for H_2O are the pure mineral or fluid, respectively, at the pressure and temperature of interest. For aqueous species, the standard-state is defined as a hypothetical one molal solution that behaves as if it is infinitely dilute. Activity coefficients of neutral aqueous species were assumed to be equal to one in the calculations. The Na and P concentrations were taken to be equal to the average of the final three sampling points of the measured AMWF concentration for all of the U24Py experiments, yielding values of $10^{-2.71}$ and $10^{-2.97}$ M, respectively. The total aqueous peroxide concentration in solution was assumed to be equal to the average total AMWF P concentration because of the 1:1 ratio of peroxide:P in the U24Py nanocluster. This ratio was deemed a better proxy for the peroxide concentration than uranium, as the precipitation of a secondary uranium phase would result in under-estimation of the peroxide concentration.

Uranium speciation was calculated by determining the activities of all aqueous species for all elements using a system of nonlinear mass action [20, 22, 23, 24] (Table S.3) and mass balance equations using a Newton-Raphson iteration program. The total uranium concentration (the sum of the individual aqueous uranium species) in equilibrium with metaschoepite as a function of pH is depicted in Fig. 7, and compared with the average of the AMWF U concentrations for the final three sampling points of each experiment. The measured AMWF U concentrations were approximately equal to or exceeded the expected solubility of metaschoepite under the experimental conditions, indicating that conditions are favorable for metaschoepite precipitation under experimental conditions. The super-saturated state with respect to metaschoepite and the deviation of the Na/U and P/U AMWF molar ratios suggests that a metaschoepite-like phase precipitated. Due to the likely presence of metaschoepite in the experimental systems, for the subsequent I.A.P. calculations, we assumed that the measured aqueous U concentrations are in equilibrium with an amorphous metaschoepite-like phase and that the isolated U24Py nanocluster in solution has the same stoichiometry as the U24Py crystalline phase reported by Ling et al. [13] of $Na_{30}[(UO_2)_{24}(O_2)_{24}(HP_2O_7)_6(H_2P_2O_7)_6]$.

3.3. Determination of Aqueous Behavior: Ion Activity Product Calculations

If the reaction for the dissolution or dissociation of the U24Py nanocluster was properly described and if U24Py nanoclusters reached equilibrium or at least a steady-state with the monomeric aqueous species in the experimental solutions, then the ion activity product can be calculated from each set of measured concentrations. The calculated I.A.P. should be equivalent to the equilibrium constant and should not vary as a function of pH or nanocluster concentration. The calculation of the I.A.P. for the U24Py nanocluster has two unknowns: 1) the reaction stoichiometry, and 2) the nature and behavior of the nanocluster in solution.

As described in the previous section, the crystalline phase stoichiometry was used to represent the stoichiometry of the isolated nanoclusters in solution, and we assumed that once the solution reached steady-state that the solution was simultaneously in equilibrium with both the isolated nanoclusters and a metaschoepite-like phase. The U24Py nanocluster could behave in solution either as a solid phase or as an aqueous complex. A solid phase would exhibit a

solubility that is independent of the concentration of the solid phase as long as the solid is present in excess. Therefore, if the dispersed U24Py nanoclusters in solution behave like a pure solid, then their activity would be equal to one, and the I.A.P. values calculated under that assumption should be equivalent to the equilibrium constant for the dissolution reaction and should be independent of pH and nanocluster concentration. In contrast, if the U24Py behaves like an aqueous complex, then the calculated I.A.P. value would only be independent of pH and nanocluster concentration when the activity or concentration of the U24Py is accounted for. The nature of the nanocluster behavior in solution was characterized by calculating the I.A.P. values using both approaches, and then determining which approach yields the lowest dependence on pH and nanocluster concentration.

The protonation state of U24Py affects the stoichiometry of the reaction between isolated nanoclusters and monomeric aqueous species, however the protonation state of the nanocluster in solution is unknown and likely varies with pH. Therefore, we initially assumed that the nanocluster is fully protonated. Subsequently, different protonation states for the nanocluster were tested as a means to yield I.A.P. values that do not change with pH or nanocluster concentration. For the purpose of calculating the I.A.P. value, a simplified stoichiometry based on a single uranyl peroxide pyrophosphate unit was used that, maintains the same stoichiometric ratios as the entire U24Py nanocluster yielding the following dissolution/dissociation reaction:

$$1.25H^+ + Na_{1.25}[(UO_2)(O_2)(HP_2O_7)_{0.25}(H_2P_2O_7)_{0.25}] \leftrightarrow 1.25Na^+ + UO_2^{+2} + H_2O_2 + 0.5P_2O_7^{-4} \quad (3)$$

The I.A.P. for Reaction (3) can be expressed as:

$$\text{I. A. P.} = \frac{a_{Na^+}^{1.25} \cdot a_{UO_2{}^{+2}} \cdot a_{H_2O_2} \cdot a_{P2O7^{-4}}^{0.5}}{a_{H^+}^{1.25} \cdot a_{\text{U24Py Nanocluster}}} \quad (4)$$

where a represents the thermodynamic activity of the subscripted species, and $a_{\text{U24Py Nanocluster}}$ represents the activity of the U24Py nanocluster in solution (see below). The I.A.P. values for Reaction (3) were calculated using a similar computational approach to that used to calculate the solubility of metaschoepite, but with the ionic strength calculated for each experiment in order to determine the activity coefficient for each species. The ionic strength was found to vary from 0.0031-0.0069 M with no systematic variation by either pH or nanocluster concentration.

The activities of the aqueous species in Eq. (4) were calculated by solving a system of nonlinear mass action (Tables S.3. and S.4.) and mass balance equations in which the total aqueous U, P, and Na concentrations were the average measured AMWF concentration from the final three sampling points for each experiment and the Li concentration was calculated from the amount added while adjusting the experimental pHs. The activity of H_2O_2 was assumed to be equal to the measured AMWF P concentration as the U24Py structure contains pyrophosphate and peroxide as integral bridging ligands. Therefore, for every mole of P liberated from the nanoclusters, a mole of peroxide would also have to be liberated. Peroxide is miscible in water and does not exsolve from the suspension at the concentrations in the experiments. Peroxide reduction was not expected to occur to a significant extent due to the short duration of the experiments and the lack of species present in the experimental systems that are readily oxidized. If the peroxide was unstable and a significant portion of the peroxide was reduced during the

experiment, then Reaction (3) would be driven to the right continually over the course of the experiments. The solutions would not have reached equilibrium or steady-state with respect to dissolved U, P, or Na, and the steady-state that we observed in the AMWF concentrations of U, P and Na after 34 days would not have occurred. The nanocluster concentration for the speciation calculations was calculated from the difference between the measured BMWF and AMWF P concentrations, which is equal to the difference between the total element and aqueous concentrations. As the experiments were conducted in an anaerobic glove box, aqueous carbonate species were excluded from the calculations.

The concentration and pH dependencies of the I.A.P. values calculated assuming the U24Py nanocluster is fully protonated with either an activity of one or an activity equal to the nanocluster concentration are shown in Figure 8. Both sets of calculated I.A.P. values show a weak concentration dependence over the examined U24Py concentration range. The I.A.P. values calculated treating the U24Py nanoclusters as an aqueous complex exhibit less of a concentration dependence (with a slope of -0.14) than the I.A.P. values calculated assuming that the U24Py behaves as a bulk solid (with a slope of -0.35). Both methods of calculating the I.A.P. values exhibit a strong pH dependence across the pH range of the experiments. The I.A.P. values calculated treating the U24Py nanocluster as an aqueous complex have a slope of -0.88; the I.A.P. values calculated treating U24Py nanocluster as a bulk solid have a slope of -0.84. The relatively large slope as a function of pH for both models indicates that the reaction as written does not properly account for the proton condition of the U24Py nanocluster, further suggesting that the nanocluster is at least partially deprotonated in solution under the experimental conditions.

We used our data to place constraints on the protonation behavior of the U24Py nanocluster in solution by determining the extent of deprotonation that is required to yield I.A.P. values that do not vary with pH or nanocluster composition. First, we tested a model in which the U24Py nanoclusters are assumed fully deprotonated and remain fully deprotonated across the pH range of the experiment. Second, we tested a model that uses a single cumulative deprotonation reaction to account for changing protonation state as a function of pH under the experimental conditions. Each pyrophosphate unit in the U24Py nanocluster has four oxygen bonds with uranyl bipyramids, leaving two terminal oxygen atoms available for protonation. Each U24Py, therefore, has 24 potential proton active sites. Ling et al. [13] determined that at least six of these sites have Na atoms bound to them, leaving 18 terminal oxygen atoms available for deprotonation. Under the assumption that the U24Py nanocluster is fully deprotonated, it would have a charge of -18 in solution, and if the Knud Thomsen formula is used to approximate the surface area of the oblate nanocluster, then the calculated charge density of the U24Py nanocluster would be 241 mC/m^2. A charge of -18 and a charge density of 241 mC/m^2 is not unreasonable for this size of nanocluster, as the charge of U60 in solution has been determined to be -19 with a charge density of 159 mC/m^2 [1]. The -18 charge of the entire U24Py nanocluster translates to a charge of -0.75 for the simplified nanocluster stoichiometry. The dissolution or dissociation reaction for the fully deprotonated U24Py nanocluster is written as:

$$2H^+ + Na_{1.25}[(UO_2)(O_2)(P_2O_7)_{0.5}]^{-0.75} \leftrightarrow 1.25Na^+ + UO_2^{+2} + H_2O_2 + 0.5P_2O_7^{-4} \quad (5)$$

Even with the use of unrealistic values for the ion size parameter å and the empirical term cI as a correction factor, Czap et al. [25] found that the extended Debye-Hückel equation fails to account for the non-ideal behavior of nanoscale tungstoaluminate polyoxometalates (POMs) in solution. POMs cannot be treated as point charges as required by Debye-Hückel theory [25-27] due to their relatively large size as compared to simple aqueous ions that the theory is based on. Therefore, for all subsequent calculations, we assumed that the activity of the U24Py nanoclusters is equal to their concentration in solution and that the nanoclusters do not contribute to the solution ionic strength.

Both the concentration and pH dependencies of the I.A.P. values are reduced when the U24Py nanocluster was assumed to be fully deprotonated (Fig. 9). The I.A.P. values that were calculated by treating the U24Py nanocluster as a bulk solid show a more significant concentration dependence (with a slope of -0.27) than those that were calculated treating the nanocluster as an aqueous complex (with a slope of -0.07). The I.A.P. values from both calculations show a significant decrease in their pH dependence when the U24Py nanocluster is assumed to be fully deprotonated compared to the fully protonated I.A.P. values. The I.A.P. values calculated by treating the U24Py nanocluster as an aqueous complex have a slope versus pH of -0.14; the I.A.P. values calculated by treating U24Py nanocluster as a bulk solid have a slope of -0.09.

The complete deprotonation of the U24Py nanocluster involves 18 proton reactive sites, where each is likely characterized by a different proton affinity and distinct acidity constant, or K_a value. Constraining the K_a value for all 18 deprotonation reactions is beyond the precision of our data. Instead we tested a model in which U24Py is not fully deprotonated across the pH range of the experiments by approximating this behavior by invoking a complete deprotonation reaction, as expressed by:

$$Na_{1.25}[(UO_2)(O_2)(HP_2O_7)_{0.25}(H_2P_2O_7)_{0.25}] \leftrightarrow 0.75H^+ + Na_{1.25}[(UO_2)(O_2)(P_2O_7)_{0.5}]^{-0.75} \quad (6)$$

where the acidity constant can be written:

$$K_a = \frac{a_{H^+}^{0.75} \cdot a_{\text{U24Py Nanocluster}_{-0.75H^+}}^{-0.75}}{a_{\text{U24Py Nanocluster}}} \quad (7)$$

where $a_{\text{U24Py Nanocluster}}$ represents the activity of the fully protonated U24Py nanocluster and $a_{\text{U24Py Nanocluster } -0.75H^+}$ represents the activity of the fully deprotonated U24Py nanocluster in solution. If the addition of Reaction (6) to the system of equations used to determine the I.A.P. values further reduces the pH dependence of the calculated I.A.P. values, then our results would suggest that the U24Py nanocluster exhibits deprotonation behavior as a function of pH. It may not exist exclusively as either fully protonated or fully deprotonated molecules, as suggested by Reaction (6). In fact, the molecule is unlikely to do so. However, the results would suggest that multiple protonation states are needed to account for the observed behaviors as a function of pH and nanocluster concentration.

For this test, we could not simultaneously solve for both the K_a value in Eq. (7) and the I.A.P. value for Reaction (3). Therefore, we used an iterative procedure to solve for the I.A.P.

values, assuming different fixed values for the K_a, and we determined which K_a value yields the least dependence of the I.A.P. value as a function of pH and nanocluster concentration. These tests reveal that the pH dependence is minimized when the K_a value is equal to -3.5.

The addition of the deprotonation reaction yields I.A.P. values with lower concentration and pH dependencies than those calculated assuming that the nanocluster is either fully protonated or fully deprotonated exclusively(Fig. 10). Treating the nanocluster as a bulk solid results in a larger slope of the I.A.P. values as a function of nanocluster concentration compared to treating the nanocluster as an aqueous complex: -0.27 and -0.07, respectively. The addition of the U24Py deprotonation reaction yields I.A.P. values for both sets of calculations that are close to being independent of the experimental pH. The slope of the I.A.P. values assuming that the nanocluster behaves as a bulk solid is -0.09, while treating the nanocluster as an aqueous complex yields a slope of -0.13.

Although neither of the calculation approaches yields I.A.P. values that are completely independent of nanocluster concentration, the approach that treats the isolated U24Py nanoclusters as aqueous complexes yields I.A.P. values that are significantly closer to being independent of nanocluster concentration than those calculated by treating the nanocluster as a bulk solid with an activity of one. In order to reduce the pH dependence of the calculated I.A.P. values, the deprotonation behavior of the U24Py nanocluster must be accounted for with the addition of a deprotonation reaction for the nanocluster. A conditional estimate of the equilibrium constant can be made by averaging all of the I.A.P. values that were calculated treating the nanocluster with a non-unit activity (Fig. 10), yielding a value of -5.0 +0.1/-0.2 (1σ) for the log equilibrium constant for Reaction 3. Our modeling results strongly suggest that the U24Py nanocluster experiences deprotonation over the experimental pH range, and that the nanoclusters are mostly deprotonated across the pH range of the experiments. Taken together, the results indicate that the aqueous behavior of the U24Py nanocluster is best described as that of an aqueous complex that undergoes sequential deprotonation as a function of pH.

Even though U24Py and U60 are both uranyl peroxide nanoclusters, we observed several differences in their aqueous behavior. In the U60 experiments [1], a steady-state between the isolated nanoclusters and monomeric aqueous species was attained within 24 hours. The U24Py experiments took over 30 days to attain a steady-state, illustrating much slower overall reaction kinetics that might be partly due to the formation of a secondary amorphous metaschoepite phase. The U24Py nanoclusters also exhibited lower stability, with an average of 72% of the total mass in the system being associated with the nanoclusters, whereas an average of over 97% was associated with the U60 nanoclusters under similar experimental conditions. The mass associated with the U24Py likely would be even lower if the U24Py experiments were conducted open to the atmosphere and subjected to the formation of uranyl-carbonate complexes as was the case in the U60 experiments. The difference between the U60 and U24Py experiments means that the reported difference in nanocluster stabilities is likely a minimum value, and direct comparison of the relative stabilities is difficult. Both types of nanoclusters are highly charged in solution. U60 exhibits a molecular charge of -19 with a charge density of 159 mC/m^2, which is caused by the leaching of Li^+ cations from the nanocluster, and the charge does not vary significantly with pH [1]. Conversely, the maximum charge of U24Py is -18 with a charge

density of 241 mC/m^2, likely caused by the deprotonation of the nanocluster, and is therefore dependent on pH. The greater charge density of the isolated U24Py nanocluster likely contributes to U24Py exhibiting a lower stability in aqueous solution than U60. However, for both U24Py and U60, the calculated I.A.P. values yield lower pH and nanocluster dependencies when treated as aqueous complexes with non-unit activities than when treated as bulk solids with activities equal to one. The results of these two studies indicate that uranyl peroxide nanoclusters such as U24Py and U60 are highly charged species when present in solution, whose aqueous behavior is best described as that of an aqueous complex. The conclusion that U24Py and U60 nanoclusters are best modeled as aqueous complexes with non-unit activities is consistent with theoretical work that has concluded that the behavior of a nanoparticle in solution is dominated by the behavior of the surface atoms [28]. As the size of a particle decreases, the proportion of surface atoms to total atoms in the particle increases to a point where the surface atoms dominate the overall chemical potential of the particle resulting in behaviors that differ from macroscopic bulk solids of the same elemental composition. Uranyl-peroxide nanoclusters such as U24Py and U60 can be considered to consist entirely of surface atoms, and hence they do not exhibit bulk solid phase behavior.

4. Conclusions

In this study, the stability and aqueous behavior of U24Py nanoclusters were determined as a function of time, pH, and nanocluster concentration. Systems with U24Py suspended in solution achieved a steady-state between the U24Py nanoclusters and aqueous monomeric species after approximately 34 days, and this steady-state was maintained for at least 14 days. The measured AMWF concentrations did not vary systematically as a function of pH or nanocluster concentration over the ranges examined. The I.A.P. values that were calculated assuming activities of the nanoclusters equal to their concentration in solution exhibit significantly lower nanocluster concentration dependence than those calculated assuming an activity of one for the nanocluster. The addition of a complete deprotonation reaction for the U24Py nanocluster minimizes the pH dependence of the calculated I.A.P. values. Our modeling results strongly suggest that the U24Py nanocluster experiences deprotonation and that the nanoclusters are mostly deprotonated across the pH range of the experiments. Taken together, the results indicate that the aqueous behavior of the U24Py nanocluster is best described as that of an aqueous complex that undergoes sequential deprotonation as a function of pH.

U24Py and U60 are just two uranyl peroxide nanoclusters in a family of more than 55 published structures. Further characterization of how nanocluster size, composition and morphology affect aqueous solution behavior is needed in order to construct general models of the behavior of uranyl peroxide and other nanoclusters, and to better understand the distribution and fate of metal and radionuclides in aqueous systems that contain nanoclusters.

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References

1. Flynn S.L., Szymanowski J.E.S., Gao Y., Liu T.; Burns P.C., Fein J.B.: Experimental measurements of U60 nanocluster stability in aqueous solution. Geochemica et Cosmochimica Acta **156**, (2015).

2. Armstrong C. R., Nyman M., Tatiana S., Sigmon G. E., Burns P. C., Navrotsky A.: Uranyl peroxide enhanced nuclear fuel corrosion in seawater. PNAS **109**, 6 (2012).

3. Burns P.C., Ewing R.C., Navrotsky A.: Nuclear fuel in a reactor accident. Science **335**, 1184 (2012).

4. Liao Z., Deb T., and Nyman M.: Elucidating self-assembly mechanisms f uranyl-peroxide capsules from monomers. Inorg. Chem. **53**, 19 (2014).

5. Miro P., Vlaisavljevich B., Dzubak A.L., Hu S., Burns P.C., Cramer C.J., Spezia R., Gagliardi L.: Uranyl-peroxide nanocapsules in aqueous solution: force field development and first applications. J. Phys. Chem. **118**, 42 (2014).

6. Wylie E.M., Peruski K.M., Weidman J.L., Phillip W.A., Burns P.C.: Ultrafiltration methods of uranyl peroxide nanoclusters for the separation of uranium from aqueous solutions. ACS Appl. Mater. Interfaces **6**, 1 (2014).

7. Sigmon G.E., Ling J., Unruh D.K., Moore-Shay L., Ward M., Weaver B., Burns P.C.: Uranyl-peroxide interaction favor nanocluster self-assembly. J. Am. Chem. Soc. **131**, 46 (2009a).

8. Sigmon G.E., Unruh D.K., Ling J., Weaver B., Ward M., Pressprich L., Simmonetti A., Burns P.C.: Symmetry verses minimal pentagonal adjacencies in uranium-based polyoxometalate fullerene topologies. Angew. Chem. Int. Ed. **48**, 15 (2009b).

9. Nyman M., Rodriguez M.A., Campana C.F.: Self-assembly of alkali-uranyl-peroxide clusters. Inorg. Chem. **131**, 17 (2010).

10. Sigmon G.E., Burns P.C.: Rapid self-assembly of uranyl peroxide polyhedral into crown clusters. J. Am. Chem. Soc. **133**, 24 (2011).

11. Qui J., Burns P.C.: Cluster of actinides with oxide, peroxide, or hydroxide bridges. Chem. Rev. **113**, 2 (2013).

12. Qui J., Ling, J., Sui, A., Szymanowski, J.E.S., Simonetti, A., Burns P.C.: Time resolved self-assembly of a fullerene-topology core-shell cluster containing 68 uranyl polyhedra. J. Am. Chem. Soc. **134**, 3 (2012).

13. Ling J., Qiu J., Sigmon G.E., Ward M., Szymanowski J.E.S., Burns P.C.: Uranium pyrophosphate/methylenediphosphate polyoxometalate cage clusters. J.A.C.S. **132**, 38 (2010).

14. Navrotsky A.: Energetics of nanoparticle oxides: interplay between surface energy and polymorphism. Geochem. Trans. **4**, 6 (2003).

15. Gilbert B., and Banfield J.F.: Molecular-scale processes involving nanoparticulate minerals in biogeochemical systems. Reviews in Minerology and Geochemistry **59**, 1 (2005)

16. Johnson K.C.: Comparison of methods for predicting dissolution and the theoretical implications of particle size dependent solubility. J. Pharmaceutical Sci. **101**, 2 (2012).

17. Kaptay G.: On the size and shape dependence of the solubility of nano-particles in solutions. Internat. J. Pharmaceutics **430**, 1 (2012).

18. Bruker: SADABS. Bruker AXS Inc., Madison, WI 2001.

19. Sheldrick, G. M.: SHELX-97 Program pack or solution and refinement of crystal structures from x-ray diffraction data, Bruker AXS, Inc. Madison, WI 1997.

20. Gorman-Lewis D., Fein J.B., Burns P.C., Szymanoski J.E.S., Converse J.: Solubility measurements of uranyl oxide hydrate phases metaschopite, compreignacite, Na-compreinacite, becquerelite and clarkite. J. Chem. Thermodynamics **40**, 6 (2008).

21. Helgeson H. C., Kirkham D. H., Flowers G. C.: Theoretical prediction of the thermodynamic behavior of aqueous-electrolytes at high pressures and temperatures. 4. Calculation of activity-coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600-degrees-C and 5 kb. Am. J. Sci. **281**, (1981).

22. Martell R.J. and Smith R.M.: NIST Critical selected stability constants of metal complexes, Version 6.0, NIST Standard Reference Database 462001, National Institute of Standards and Technology; Gaithersburg, MD 2001.

23. Guillaumont R., Fanghanel T., Fuger J., Grenthe I., Neck V., Palmer D., Rand M.: Updated on the Chemical Thermodynamics of Uranium, Neptunium and Plutonium, second ed., Elsevier; Amsterdam 2003.

24. Zaninato P.L., Di Bernardo P., Grenthe I.: Chemical equilibria in the binary and ternary uranyl(VI)-hydroxide-peroxide systems. Dalton Trans. **41**, 12 (2012).

546 25.Czap A., Neuman N.I., Swaddle T.W.: Electrochemistry and homogeneous self-exchange
547 kinetics 12-tungstoaluminate (5-/6-) couple. Inorg. Chem. **45**, 23 (2006).

548 26. Liu, T.B.: Hydophillic Macroionic Solutions: What happens when soluble ions reach the size
549 of nanometer scale? Langmuir **26**, 12 (2010).

550 27. Haso F., Fang X., Yin P., Ross J.L., Liu T.: The self-assembly of a macroion with anisotropic
551 surface charge density distribution. Chem. Commun. **49**, 6 (2013).

552 28. Rusanov A. I., Shchekin A.K.: On the formulation of the material equilibrium condition for a
553 dissolving solid nanoparticle. A.I.P. **127**, 19 (2007).

Figure 1. Schematic of experimental filtration process. 1) 0.2 μm PTFE membrane used to test for secondary microscale particulates. 2) 3,000 Da molecular weight filter to separate the nanocluster from the monomeric aqueous species. All samples were divided into two portions for the analysis of U, P and Na: (A) Before molecular weight filtration (BMWF) which measured the element concentrations after filtration step 1, but before filtration step 2; and (B) the After molecular weight filtration (AMWF) which measured the element concentrations after molecular weight filtration, step 2.

Figure 2. Representative electrospray mass spectroscopy spectra plotted on an arbitrary y-axis. The spectrum from the BMWF sample is represented by the solid curve, and the spectrum from the AMWF spectrum is represented by the dashed curve.

Figure 3. An example of U24Py nanocluster partitioning experiments from experiment S22, conducted under the following conditions: pH 8.7 and 2.86 g/L U24Py. Remaining experimental data are shown in the Supplemental Information section. **A)** BMWF concentrations of U, P, and Na; **B)** AMWF concentrations of U, P, and Na.

Figure 4. Measured AMWF **A)** U, **B)** P, and **C)** Na concentrations from all experiments. Each data point represents the average concentration of the final three data points for a particular experiment. A, B, and C are plotted as a function of final solution pH for U, P, and Na, respectively.

Figure 5. Measured AMWF **A)** U, **B)** P, and **C)** Na concentrations from all experiments. Each data point represents the average concentration of the final three data points for a particular experiment. A, B and C are plotted as a function of initial nanocluster concentration in each experiment for U, P and Na, respectively.

Figure 6. The calculated AMWF **A)** Na/U and **B)** P/U molar ratios from all experiments. Each data point represents the molar ratio calculated from the average concentration of the final three data points for a particular experiment.

Figure 7. The average AMWF uranium concentrations in the final three data points from each experiment (○) plotted with the calculated solubility of metaschoepite as the solid curve.

Figure 8. Calculated I.A.P. values assuming the U24Py nanocluster is fully protonated. The diamonds represent the I.A.P values calculated by treating the nanoclusters as a solid phase with an activity of one. The circles represent the I.A.P. values calculated by treating the nanoclusters as aqueous complexes with an activity equal to the nanocluster concentration in solution. **A)** I.A.P. values as a function of nanocluster concentration. **B)** I.A.P. values as a function of pH. Lines are linear best-fits of each set of values.

Figure 9. Calculated I.A.P. values assuming the U24Py nanocluster is fully deprotonated as a function of: **A)** nanocluster concentration; and **B)** pH. Lines are linear best-fits of each set of values. Data symbols are the same as in Figure 8.

Figure 10. Calculated I.A.P. values incorporating a U24Py deprotonation reaction in the calculations. **A)** I.A.P. values as a function of nanocluster concentration **B)** I.A.P. values as a

592 function of pH. Lines are linear best-fits of each set of values. Data symbols are the same as in
593 Figure 8.