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Sonochemistry of Actinides

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Introduction

Scientists have long known that hydrogen gas and hydrogen peroxide are formed as a result of power ultrasound on water or aqueous solutions. This early research served to establish what was then a new field of chemistry known as “sonochemistry.”

In general, ultrasound spans frequencies of roughly 15 kHz to 1 GHz. However, sonochemical effects are observed only in the range of 15 kHz to 2 MHz. Higher frequency ultrasound is used principally for medical and material diagnostics. The acoustic wavelengths of chemically active ultrasound ($1-10^{-4}$ cm) are much higher than the molecule size. Therefore, sonochemistry does not arise from a direct action of ultrasonic waves on molecules but rather from the acoustic cavitation phenomenon. Simply put, cavitation is a set of consequent events: nucleation, growth, and implosive collapse of microbubbles reaching a resonance size in applied cavitation field. Scientists generally agree that the chemical and physical effects of ultrasound are related to the extremely rapid implosion of cavitation bubbles.

We must emphasize that acoustic cavitation leads not only to the chemical transformation of the medium but also to light emission known as sonoluminescence. Recent spectroscopic studies of sonoluminescence discovered the formation of nonequilibrium plasma inside the collapsing bubble. The photons and “hot” particles produced by the sonochemical plasma may excite nonvolatile species in solutions, thus increasing their chemical reactivity.

In principle, each cavitation bubble serves as a plasma chemical microreactor that provides highly energetic processes to the bulk solution at almost room temperature. In heterogeneous systems, the mechanical forces generated by cavitation—rather than the chemical effects—could play a much more important role. At the vicinity of a solid boundary, the bubble collapse becomes asymmetric and leads to several specific phenomena, such as acceleration of mass transfer, surface erosion, and grain-size reduction. Today, using power ultrasound to enhance the reactivity of solids has become a routine technique in a large set of processes.

Over the past few years, the sonochemistry group at the Institute for Separation Chemistry in Marcoule (ICSM) has performed research dedicated to the fundamental understanding of actinide and lanthanide chemistry under ultrasound irradiation. The first sonochemical reactions of actinides in aqueous solutions were reported more than 20 years ago. In most cases, there is no direct action of cavitation bubbles on the actinide species. Instead, ultrasonic irradiation causes a chemical transformation of the liquid medium, followed by redox interactions of the sonolytic products with actinide ions. For example, sonolysis of nitric acid solutions yields as principal products nitrous acid, HNO_2 , in the liquid phase, and NO_x in the gas phase.

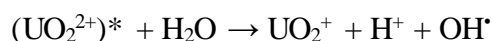
Unlike in pure water, H₂O₂ formation is not observed in nitric acid solutions because of its rapid scavenging with HNO₂. In nuclear chemistry, nitrous acid is known as a key reagent that determines the redox kinetics of actinides in nitric acid solutions. Therefore, ultrasonic treatment seems suitable in controlling the actinide oxidation states without having to add any side chemicals. This report summarizes the most recent data on sonoluminescence of uranium and redox reactions of plutonium under the effect of acoustic cavitation. This work results from a strong collaboration between the ICSM/LSFC and the DEN/DRCP departments of Marcoule Research Centre.

Fundamental Sonochemistry of f-Elements: Sonoluminescence of Uranyl Ion

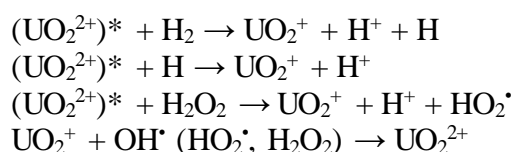
Excited uranyl ions are known for their green fluorescence. Such ions have been used for more than 150 years for dyeing glasses and performing analyses. Because they are strong oxidants (E₀= 2.6 V vs. NHE), they are of particular interest for use in radioactive waste management, as they can oxidize organic substrates in radioactive liquid wastes. The redox properties of these ions can also be used to develop advanced actinide separation processes.

New approaches to excite uranyl ions are of particular interest today. So far, excitation pathways of uranyl ions involve UV/Vis light and radiolysis of liquid or solid systems containing uranium. Ultrasound presents similarities with both methods. Indeed, a plasma is formed during the violent collapse of cavitation bubbles. First, it emits light (sonoluminescence) that spans from the UV to the NIR, possibly photoexciting the uranyl ions. And second, formed in the bubbles are hot particles, which may excite species in solutions by collisions at the bubble-solution interface. The excitation of uranyl ions under the effect of 20-, 203-, and 607-kHz ultrasound was investigated experimentally in acidic solutions of HClO₄ and H₃PO₄. Interestingly, although in HClO₄ solutions uranyl ions exhibit extremely weak sonoluminescence, their emission in H₃PO₄ is extremely bright—it is even visible to the naked eye (Fig. 1).

A first explanation of this difference is the existence of a strong quenching of UO₂^{2+*} by water molecules, either by vibrational coupling or by the abstraction of a hydrogen atom from a water molecule coordinated to uranium:



In H₃PO₄, uranyl ions are protected by complexation. Besides, an additional source of quenching was observed, one that is ultrasound-specific: quenching by sonolytical products (H₂, H₂O₂), whose formation rates also decrease in the presence of uranyl ions. The suggested mechanism is the following:



After observing uranyl bright sonoluminescence in H₃PO₄, we investigated its mechanism of excitation by varying the concentration of UO₂²⁺. If the mechanism is photoexcitation, we expected that the intensity of uranyl luminescence should vary linearly with its concentration. On the other hand, we expected in the collisional excitation mechanism that uranyl's reciprocal light emission would vary linearly with the reciprocal UO₂²⁺ concentration. Our

experiments show that sonophotoluminescence dominates in diluted solutions, and that collisional excitation adds its contribution at higher UO_2^{2+} concentration ($[\text{UO}_2^{2+}] > 0.035 \text{ M}$).

Sonochemistry in Homogeneous Media: Redox Behavior of Plutonium Ions

The sonochemical adjustment of the actinide oxidation states in solution may represent an original and interesting alternative to conventional processing methods. Accurate tuning of the experimentation parameters enables the sonication of aqueous solutions to generate in situ redox species with controlled kinetics without having to add salt or a concentrated reagent to the solution. Oxidant or reducing species therefore may be generated as a function of the required solution chemistry.

Figure 2 illustrates one of the sonochemical setups in a glovebox available at Atalante facility in Marcoule. It is in such a reactor that there have been studies about the sonochemical behavior of plutonium ions in aqueous nitric solutions. In a 1 M nitric medium, we observed the rapid and catalytic oxidation of Pu(III) to Pu(IV) (followed by absorption spectroscopy, respectively at 602 and 476 nm). Such oxidation is attributed to nitrous acid generation as a result of nitric acid sonolysis.

Very stable in sonicated 1 M nitric acid, Pu(IV) can be reduced to Pu(III) in the additional presence of 0.1 M antinitrous reagents (Fig. 3). The reduction process follows a first-order reaction law whatever the reactant: with $k' = 5.7 \cdot 10^{-3} \text{ min}^{-1}$ in the presence of sulfamic acid (at 0.45 W.mL^{-1}), with $k' = 7.5 \cdot 10^{-3} \text{ min}^{-1}$ in the case of hydrazinium nitrate (at 0.52 W.mL^{-1}). The slight reported difference on the apparent rate constants results from the additional reducing property of hydrazinium nitrate towards Pu(IV). Note also that the Pu(IV) reduction rate increases with applied acoustic pressure and that the reduction process is uncompleted—it remains a steady state in which Pu(III) and Pu(IV) exhibit constant concentrations for extended sonolyses (Fig. 3).

Furthermore, no additional redox states of plutonium are observed in solution during Pu(IV) sonolysis under these conditions. The absence of H_2O_2 in solution during sonication suggests its contribution in the reduction process which agrees with plutonium's classical solution chemistry. By sonicating a Pu(III) solution in 1 M HNO_3 - 0.1 M $[\text{N}_2\text{H}_5][\text{NO}_3]$, we noticed the accumulation of Pu(IV) in solution. We therefore attributed the observed steady state (for extended sonolyses) to the partial back oxidation of Pu(III) with sonochemically generated H_2O_2 . Indeed, H_2O_2 can be considered as both an oxidizing (1.77 V vs. NHE for $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ couple) and a reducing agent (0.68 V vs. NHE for $\text{O}_2/\text{H}_2\text{O}_2$ couple).

These overall redox processes agree with what has been observed in the literature without ultrasound (Fig. 3's insert). Note that reducing Pu(IV) is supposed to occur by forming soluble peroxy complexes that decompose in acidic media to form Pu(III). However, these complexes were not observed in our experimental conditions, possibly because of their low amount and instantaneous decomposition.

This study demonstrates that the in situ generation of reactive species provided by high-power ultrasound may help stabilize actinide redox states without adding chemicals during the process. Although observed with low rates, the considered kinetics may be optimized with appropriate settings for frequencies, concentration of solutes, gaseous atmosphere, presence of catalysts, etc.

Sonochemistry in Heterogeneous Systems: Sonochemical Preparation of Plutonium Intrinsic Colloids

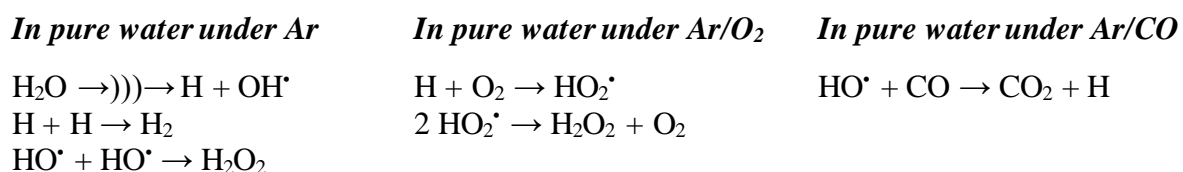
Fundamentally understanding colloid formation and its characterization today play a critical role in actinide chemistry because of environmental concerns related to contamination, waste disposal, and migration in the environment. Industrial separation processes (e.g., PUREX) also generate actinide colloids during equipment cleaning. Beneficial to such companies would be a predictive model that describes colloid behavior, formation, and subsequent separation.

Pu(IV) is particularly prone to hydrolysis (even under very acidic conditions), which further leads to intermolecular condensation reactions and the formation of multinuclear metal oligomers. We showed that the extended sonication of PuO₂ (180 mg, calcinated at 600°C, S_{BET}= ~10 m².g⁻¹) under argon atmosphere in pure water leads (after centrifugation to remove big PuO₂ particles) to the formation of intrinsic colloids that are stable for several months.

We compared these colloids to classical hydrolytic colloids obtained by diluting in pure water a known concentration of Pu(IV) initially stored in nitric acid. Besides the different green color tones (Fig. 4), the resulting Vis-NIR absorption spectra indicate that both colloids show some structural similarities but also some significant differences, including a strong Mie scattering for the sonolytic colloid resulting possibly from the presence of larger aggregates. Among the various oxides studied in our lab (CeO₂, ThO₂, etc.), PuO₂ is the only material having such a behavior under acoustic cavitation.

Although sonication in heterogeneous systems is known to increase erosion of surfaces and fracturation of grains, complementary experiments performed with ThO₂ emphasized that the mechanical action resulting from acoustic cavitation is not responsible for forming plutonium colloids. Therefore, we considered chemical reactions driven by acoustic cavitation, and we surprisingly observed that plutonium colloid formation highly depends upon the gaseous atmosphere during sonication. In the presence of Ar/O₂ (80/20, v/v), plutonium colloids are not observed, whereas an increased rate of formation is observed under Ar/CO (90/10, v/v). Previous investigations showed that this phenomenon results from the ability of these gases to favor the generation of either H₂ or H₂O₂.

In pure argon, the sonolysis of pure water leads to the homolytic dissociation of H₂O, followed by the recombination of the formed radicals to H₂ or H₂O₂. In the presence of an Ar/O₂ mixture, O₂ can react with hydrogen radicals and decrease dramatically the generation of H₂ while H₂O₂ is increased. By contrast, OH radicals may be scavenged under a CO atmosphere and thus favor the formation of H₂. The main related reactions are summarized as follows:



In conclusion, plutonium colloid formation is most likely governed by a redox mechanism and results from sonochemically induced reactions in which H₂ first reduces Pu(IV)_s to Pu(III)_l. The local transient heating driven by bubble collapse at the solid/liquid interface may

possibly activate this process. Pu(III) is then oxidized in solution by remaining $\text{OH}^\cdot/\text{H}_2\text{O}_2$ species, yielding Pu(IV) colloids. Although Pu(IV) colloids are generally reported as highly charged polynuclear species with coordinated anions originating from electrolyte salts, we show in this work that high-power ultrasound may provide the opportunity to prepare stable colloids without any salts or stabilizing agents, which is of paramount interest in the study of their behavior.

Conclusion

The few examples outlined in this article bring to light some of the actinide activities performed by the sonochemistry group in Marcoule. Such work demonstrates the potential and diversity of applying sonochemistry in the actinide area. Of particular interest to nuclear chemistry is the possibility of generating in situ active species without adding side chemicals. In nuclear chemistry, dilution of solutions should be avoided because of hydrolysis concerns. Sonication also contributes to the generation of smaller volumes of effluents—this is particularly attractive in nuclear reprocessing (e.g., waste amounts, concentration of feed solutions).

Experimental parameters (such as field intensity, applied frequency, carrier gases, and concentration of solutions) offer a large field of applications that could contribute to efficient and specific chemical systems. Large-scale ultrasonic devices are available today for high volumes with a huge amount of reliable possibilities, such as batch or continuous processing, multifrequencies, coupling with other techniques, and noncontact sonication. In this sense, the fundamental understanding of the acoustic cavitation and related sonochemistry has to be further studied to improve kinetics and propose future directions.

Further Reading

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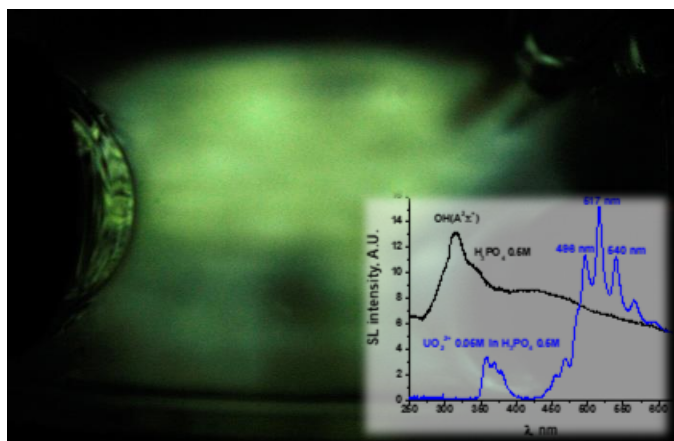


Fig. 1. This photo shows the sonoluminescence of a solution of 0.05 M UO_2^{2+} in 0.5 M H_3PO_4 , sonicated at 203 kHz (35 W, 10°C) under argon flow. The inset shows the corresponding sonoluminescence spectra with that of the pure acid.



Fig. 2. This experimental setup was used to perform 20-kHz sonochemical experiments at the Atalante facility in Marcoule. This device consists of a tight reactor that can control temperature, a circulation of carrier gases, and even the sampling of solution during sonolyses. The cell is cooled from outside the box and an UV-Vis-NIR spectrophotometer is also connected to the enclosure.

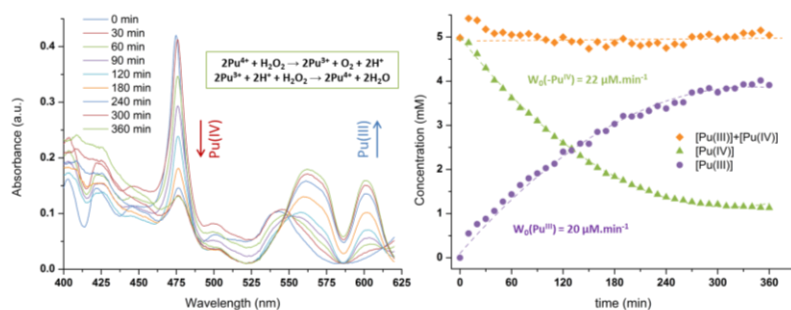


Fig. 3. The image on the left shows UV-Vis absorption spectra measured during the sonication of a Pu(IV) solution in 1 M HNO_3 – 0.1 M $\text{NH}_2\text{SO}_3\text{H}$. The image on the right shows plotted concentrations measured for Pu(IV) and Pu(III) in similar conditions (at 476 and 602 nm, respectively). The left figure's insert shows the overall chemical reactions that occur under sonication. These reactions agree with the literature with respect to corresponding experiments without ultrasound.

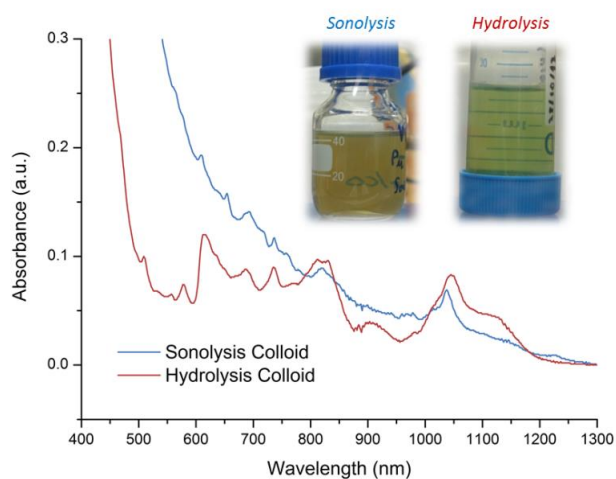


Fig. 4. This figure shows Vis-NIR absorption spectra observed for “hydrolysis” and “sonolysis” colloids. Hydrolysis colloids were obtained by diluting Pu(IV) in pure water (final concentration: $7\text{--}9 \times 10^{-3}$ M). Sonolysis colloids were obtained by sonicating (20 kHz, argon, $0.34 \text{ W}\cdot\text{mL}^{-1}$) 180 mg of PuO_2 in 50-mL H_2O (followed by centrifugation at 9000 rpm, with a final concentration of $\sim 1.5 \times 10^{-3}$ M). The insert shows the pictures of these colloids.