

Characteristics of U(IV) Nanoparticles and Their Interactions with Natural and Synthetic Macromolecules in Aqueous Solutions

Wansik Cha*, Sun Tae Kim, Deok Beom Seo, Hye-Ryun Cho, Euo Chang Jung
Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute,
989-111 Daedeok-daero, Yuseong-gu, Daejeon, 34057, Republic of Korea

*Corresponding author: wscha@kaeri.re.kr

1. Introduction

In subsurface groundwater systems colloidal nanoparticles (NPs) are considered as potential carrier phases of radionuclides (RNs) influencing the migration behaviors of RNs in groundwater environment. Under reducing conditions tetravalent uranium (U(IV)) is known to form solid phases such as U(IV) hydrous oxide ($\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$) and crystalline U(IV) ($\text{UO}_2(\text{cr})$) precipitates as well as UO_2 -like intrinsic colloidal NPs in near neutral aqueous solutions due to its low solubility. The U(IV) NP formation process is one of key steps in mineralization or immobilization of uranium which can be mediated either by microbes or by abiotic geochemical reactions [1].

In our previous study the mechanism of U(IV) NP formation and the involvement of reaction intermediates were proposed [2]. The results demonstrate that the NP formation process is very sensitive toward temperature variation. The reaction kinetics exhibits an autocatalytic nature for consuming $\text{U}(\text{OH})^{3+}$ in its supersaturated solution at a mildly acidic pH (2~3). We also suggested that during this conversion process the intermediate species provide reactive or catalytic reaction sites likely at the terminal of the structure or the surface of primary NPs. However, the U(IV) NPs prepared as described in our study turned out to be unstable at neutral pH and form black precipitates.

Thus, in this study we further demonstrate that the stability of U(IV) NPs can be enhanced by using synthetic and natural organic macromolecules. The characteristics of the stabilized U(IV) NP was examined using various analytical techniques including UV-Vis absorption and FTIR spectroscopy, dynamic light scattering (DLS) analysis, nanoparticle tracking analysis (NTA) and transmission electron microscopy (TEM). The detailed pictures of macromolecular interaction at the NP-water interface are discussed to explain the stability of NPs in aqueous solutions.

2. Experimental

A U(IV) stock solution (pH 0.3) was prepared by electrochemically reducing a stock solution of U(VI) using Hg/Pt electrodes, as described in [3]. The U(IV) NP solutions were prepared by heating aqueous U(IV) sample solution in the presence or absence of macromolecules such as polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA) and humic acid (HA) under mildly acidic and anaerobic (i.e., Ar-purged) conditions.

Absorption spectra of the U(IV) solutions were measured using a dual-beam UV-Vis spectrophotometer (CARY 3E, Varian, Palo Alto, CA) and quartz cuvette cells of 1-cm or 1-mm optical pathlength (Hellma, Germany). All spectra were measured at a controlled temperature ($\pm 0.1^\circ\text{C}$) using a Peltier-controlled 6-cell cuvette holder (qChanger6, Quantum Northwest, WA). To investigate the interactions of macromolecule's functional groups with NPs the changes in FTIR spectra of NP-containing sample solutions were monitored using attenuated total reflection (ATR)-FTIR spectrometer (Nicolet, iS50). All spectral baselines were corrected for quantitative estimation of the participation of macromolecule's functional groups in surface adsorption or complexation on NPs. DLS (Zetasizer Nano, Malvern Inst., UK) and NTA (Nanosight LM10, Malvern Inst., UK) techniques were employed to directly measure the size distribution, zeta potential and concentration of NPs in the sample solutions. The particle size, morphology and crystalline structures of dry U(IV) NPs were measured from TEM image analysis (JEM 2100-F, JEOL).

3. Results and Discussion

3.1 Effects of solution pH on the stability of U(IV) NP.

Under a mildly acidic condition (pH > ~2) the concentration of U^{4+} is very low and $\text{U}(\text{OH})^{3+}$ is the major dissolved U(IV) species. Formation of a solid phase, $\text{UO}_2(\text{cr})$ is predicted based on the reported thermodynamic data of U(IV) solubility and hydrolysis [4]. However, in the previous study we reported that $\text{UO}_2(\text{cr})$ formation is kinetically hindered at temperatures lower than room temperature [2]. It is demonstrated that at an elevated temperature U(IV) NP formation can be facilitated and spectrophotometrically analyzed by monitoring the consumption of $\text{U}(\text{OH})^{3+}$ in the solution.

The U(IV) NPs obtained in this way are found to be quite stable in a mildly acidic solution in terms of the colloidal particle size distribution, e.g., for weeks at room temperature and for months at lower temperatures. At pH 2-3 the U(IV) NP solution exhibits a positive zeta potential value, approximately +30-40 mV. This indicates that the surface or the terminal structure is positively charged likely with coordination of hydroxyl ligand, i.e., $(\text{U}(\text{O})_x(\text{OH})_y)_n$ ($x < 2$). Thus, the electrostatic repulsion among particles is thought as the primary mechanism of the U(IV) NP stability in a low pH aqueous solution.

3.2 Interactions of macromolecules with U(IV) NP

The U(IV) NPs were synthesized in the presence of macromolecules such as PVP, PVA and HA. Since most of HA is insoluble at low pH, the effects of HA was examined after the preparation procedure and by adding an aliquot of its stock solution into near neutral aqueous NP samples. The overall sizes of the NP clusters prepared in the presence of PVP and PVA were measured to range from approximately 30 nm to 80 nm by using DLS and NTA methods. Zeta potential values are found close to zero, or slightly negative values. Although such changes of zeta potential normally accompany adverse effects on colloidal stability, these NPs exhibit good dispersion stability even in neutral aqueous solutions. The TEM analysis result in Fig. 1 indicates that the individual NP cluster is well separated from each other with a spacing likely regulated by the layer of macromolecules in between.

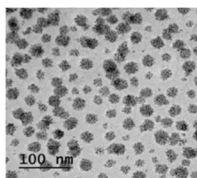


Fig. 1. TEM image of U(IV) NP clusters prepared in the presence of PVP. The primary NP size is approximately 2-3 nm as prepared at elevated temperature (80-90 °C) in 5 h.

The effects of macromolecules on the NP stability were further analyzed by using various analytical techniques. For PVP, ATR-FTIR analysis was employed to monitor the changes of FTIR spectra, particularly in the region of carbonyl (C=O) stretching bands (1600-1700 cm^{-1}). As shown in the normalized FTIR spectra of Fig. 2, a new carbonyl band appears in the lower frequency region ($\sim 1570 \text{ cm}^{-1}$) when PVP is added into the U(IV) NP solution. This indicates that the PVP-mediated stabilization effect involves a direct binding of PVP to U(IV) on the surface of NPs, i.e., a chemisorption via carbonyl oxygen. With increasing the NP:PVP ratio, the normalized intensity of the new band also increases owing to the less contribution of carbonyl groups from free or unbound PVP. Thus, PVP serves not only as a simple dispersant but also as a macro-ligand chemically interacting with U(IV) NPs.

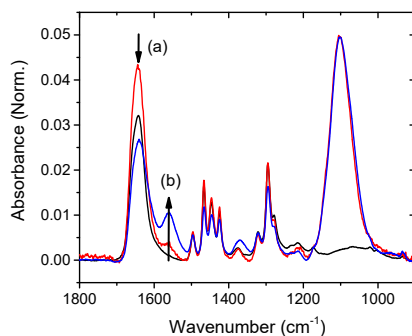


Fig. 2. ATR-FTIR spectra of PVP (0.5 %) and U(IV) NP-PVP mixed solutions (0.25% PVP, [U(IV)] = 2.4 mM and 5.0 mM) (a) original carbonyl bands from PVP and (b) new bands emerging in the presence of U(IV) NPs.

In order to study the effect of HA the zeta potential and the particle size distribution of U(IV) NP were measured by increasing the amount of HA at neutral pH. The results show that the zeta potential shifts to more negative values as the HA concentration increases in the U(IV) solution. In addition, the overall particle size of NP slightly increases. Based on these results it is proposed that HA creates an additional layer possessing a negatively charged, or electrostatic characteristics, therefore it can further stabilizes NPs.

4. Conclusions

This study shows that the stability of U(IV) NPs is pH-dependent. The NPs are unstable and form a precipitate in neutral aqueous solutions although in an acidic solution their particle size distribution is maintained for long time below room temperature. The presence of water-soluble macromolecules such as PVP and HA results in enhancing the stability of U(IV) NP at near neutral pH regions. It is demonstrated that these substances can prevent NP agglomeration by serving as a macro-ligand forming inner sphere-like complex structures and sterically separating the individual NPs, or by adding electrostatic (charge repulsion) characteristics on the surface of NPs. In the presentation the proposed NP stabilization mechanism will be discussed in detail.

ACKNOWLEDGEMENTS

This work was financially supported by the Nuclear Research and Development program of the National Research Foundation of Korea (grant code: 2017M2A8A5014719).

REFERENCES

- [1] D. R. Lovely and J. D. Coates, Bioremediation of Metal Contamination, Current Opinion in Biotechnology, Vol. 8, pp. 285-289, 1997.
- [2] W. Cha, H.-R. Cho, E. C. Jung, Formation of U(IV) Nanoparticles and Their Growth Mechanism in Mildly Acidic Aqueous Phases, Korean Nuclear Society Spring Conference, May.12-13, 2016, Jeju, Korea.
- [3] D. Cohen and W. T. Carnall, Absorption Spectra of Uranium(III) and Uranium(IV) in DClO_4 Solution, Journal of Physical Chemistry, Vol. 64, pp. 1933-1936, 1960.
- [4] V. Neck, J.I. Kim, Solubility and Hydrolysis of Tetravalent Actinides, Radiochimica Acta, Vol. 89, pp. 1-16, 2001