

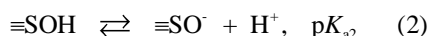
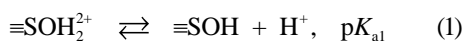
Surface Reactivities of U(IV) Nanoparticles in Aqueous Phases

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1. Introduction

Reduced forms of radionuclides such as tetravalent uranium (U(IV)) are prevalent under deep geological conditions. In such anoxic environment U(IV) exists mostly in solid forms in near neutral aqueous solutions, such as U(IV) hydrous oxide ($\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$) and crystalline precipitates ($\text{UO}_2(\text{cr})$) due to its low solubility. Natural occurrence of U(IV) nanoparticles (NPs) should be considered, which is known to be mediated either by microbes or by abiotic geochemical reactions [1]. Colloidal NP in groundwater system is a potential carrier phase influencing radionuclide migration in subsurface environment. Recently, colloid-facilitated transport is accepted as one of main radionuclide migration mechanisms from contaminated sites such as acid mineral mines, spent fuel storage facilities and weapon test sites. Therefore, it is important to understand the behaviors of colloidal particles and the factors affecting their stability.

The colloidal stability of U(IV)-NPs can be described in terms of inter-particle electrostatic charge repulsion preventing colloid aggregation. Thus, the surface charge of particles and the concentration of solution components such as pH and ionic strength are important variables. In addition, their surface charge distribution depends on pH owing to the amphoteric nature of U(IV)-NP surface as observed in $\text{UO}_2(\text{s})$ and other mineral oxides. If the surface charge approaches zero, dispersions of U(IV)-NPs are expected to be destabilized. The pH point of zero charge (pH_{pzc}) is an indicative parameter showing the surface acidity as well as the surface reactivity toward complexing ligands present in aqueous phases. Surface complexation models specifically defining surface species and their reactions enable a molecular description of surface reactions. For example, by adopting a two- pK_a model, the surface charge changes can be described as rxns. (1) and (2), where $\equiv\text{SOH}$ is the surface species. Then, the pH_{pzc} then can be related to those two pK_a values, i.e., $\text{pH}_{\text{pzc}} = (\text{pK}_{a1} + \text{pK}_{a2})/2$.



In this study, we attempted to evaluate the surface acidity of aqueous U(IV)-NPs using acid-base potentiometric titration method. In previous studies, we explored the adsorption behaviors of p-nitrocatechol (nCA, an 1,2-dihydroxybenzen ligand) on U(IV)-NPs [2].

Based on the surface acidity data obtained above, we further applied a surface complexation model to interpret the nCA surface adsorption behaviors.

2. Experimental

The aqueous stock solution of U(IV) was obtained by electrochemical reduction of U(VI) using Hg/Pt electrodes as described in [3,4]. The test solutions of U(IV)-NPs were synthesized as reported in our previous works [3,4]. All sample preparations and experiments were carried out in an anoxic Ar-filled glove box.

The dynamic light scattering (DLS) and nanoparticle tracking analysis (NTA) (Zetasizer Nano and Nanosight LM10, respectively, Malvern Instrument, UK) techniques were employed to directly measure the size distribution, ζ (zeta)-potential and concentration of NPs in the sample solutions. The morphology of dry U(IV)-NPs was measured from transmission electron microscopy (TEM) image analysis (JEM 2100-F, JEOL).

For potentiometric titration experiments, the acidity of an initial solution was adjusted to pH 3 as taken from the U(IV)-NPs stock solution. This solution was divided, for example, to make twelve samples, each of 16 mL volume in separate vessels. Then, different amounts of basic solution aliquots (titrant, 0.5 M NaOH) were added in to each vessel above to give different final pH. Finally, the mixed solutions were equilibrated for at least 24 h in an Ar-filled glove box before pH measurement. The titration curves were analyzed by using reaction data optimization programs including Hyperquad2013 of Protonic Software (UK). Further, Phreeqc (ver. 3) and PEST programs were utilized to simulate the nCA surface complexation model based on the previously examined adsorption data on U(IV)-NPs.

3. Results and Discussion

3.1 Colloidal characteristics of U(IV)-NPs in aqueous solution

The synthetic U(IV)-NPs have a characteristic morphology; their nominal size in stock solutions is 25-35 nm as measured by DLS analysis and their individual particle is in fact a cluster or an aggregate of smaller primary particles having crystalline uraninite(UO_2)-like structure (3-6 nm) as shown in Fig. 1. In aqueous solutions these particles exhibit dynamic colloidal behaviors depending on pH and nCA concentration as demonstrated in Table I. The ligand-free U(IV)-NPs

show typical amphoteric behaviors; the measured ζ -potential values change from positive to negative values as the solution pH increases from 2 to 10. Lower values of ζ -potential of the intact NPs indicate destabilization of particle colloids, which results in the further aggregation of particles and the particle size increase to 1-2 μm . However, the presence of nCA in solutions induces the surface potential decrease to negative values because of the surface complex formation. Such effects are more prominent at $\text{pH} > 6$ enough to stabilize the NPs and make homogeneous colloidal suspensions.

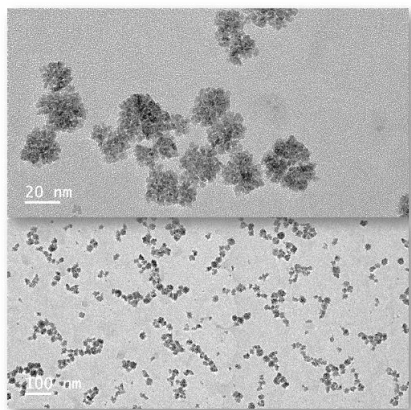


Fig. 1. TEM images of U(IV)-NPs taken from an acidic aqueous solution ($\text{pH} 2$).

Table I: Colloidal properties of U(IV)-NPs depending on pH and nCA concentration.

	pH 2	pH 6	pH 10
$[\text{nCA}] = 0 \text{ mM}$			
ζ -potential (mV)	+32	0	-8.5
Particle size (nm)	31	~ 1600	~ 1800
$[\text{nCA}] = 1 \text{ mM}$			
ζ -potential (mV)	-10	-31	-29
Particle size (nm)	~ 2900	35	29

3.2 Estimation of surface acidity and reactivity

To estimate the surface acidity of the aqueous U(IV)-NPs the acid-base titration profiles as shown in Fig. 2 were analyzed by applying non-electrostatic two- pK_a surface complexation model. From this analysis, the pK_a values of rxns. (1) and (2) were obtained, which are approximately 4.5 and 7.0 for pK_{a1} and pK_{a2} , respectively. In addition, the surface species distribution can be estimated. The solid lines in Fig. 2 display the consecutive evolution of $\equiv\text{SOH}_2^+$, $\equiv\text{SOH}$ and $\equiv\text{SO}^-$ species as the titration proceeds from acidic pH. Based on the acidity model the calculated pH_{pzc} is found approximately at $\text{pH} 5.8$. This pH_{pzc} value is close to the value reported in the literature [5], and the isoelectric point (~ 6.2) estimated in this study from the ζ -potential data.

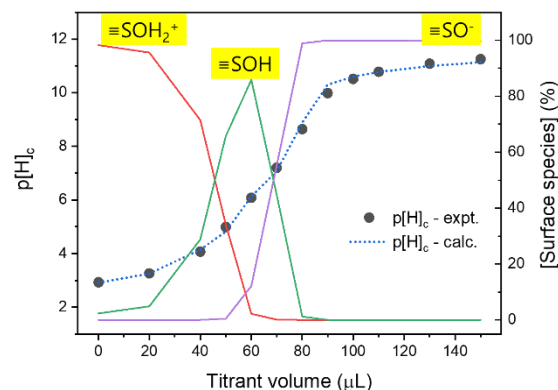


Fig. 2. Analysis of potentiometric titration results using non-electrostatic two- pK_a model ($[\text{U(IV)-NPs}]_{\text{total}} = 10 \text{ mM}$, $[\text{NaOH}]_{\text{titrant}} = 0.5 \text{ M}$).

Such analytical results were further employed to interpret the nCA adsorption equilibria on U(IV)-NPs. In the previous study, we showed that nCA adsorption data was well fitted to the Langmuir isotherm model [2]. Herein, for the nCA surface binding we propose to use two types of surface complex formation reactions, in which formation of bidentate chelate structure is assumed based on various spectroscopic evidences. More details of surface complexation analysis for nCA adsorption will be provided in the presentation.

3. Conclusions

One of major factors determining the colloidal stability of U(IV)-NPs is the surface charge distribution which is dependent on solution pH. Based on potentiometric titration results we estimated the surface acidity of U(IV)-NP's surface sites. Finally, based on our previous nCA adsorption studies, a surface complexation model was also suggested, which we believe is useful to understand the colloidal behaviors of U(IV)-NPs and their stability in aqueous solutions.

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