

Research Article

Probing Uranium(IV) Hydrolyzed Colloids and Polymers by Light Scattering

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Tetravalent uranium readily undergoes hydrolysis even in highly acidic aqueous solutions. In the present work, solutions ranging from 0.4 to 19 mM (total U) concentration ($1 < \text{pH} < 4$) are carefully investigated by light scattering technique with special emphasis on polymerization leading to colloid formation. The results clearly indicate that the concentration has significant effect on particle size as well as stability of colloids. With increasing concentration the size of colloids formed is smaller due to more crystalline nature of the colloids. Stability of colloids formed at lower concentration is greater than that of colloids formed at higher concentration. Weight average molecular weight of the freshly prepared and colloidal polymers aged for 3 days is determined from the Debye plot. It increases from 1,800 to 13,000 Da. 40–50 atoms of U are considered to be present in the polymer. Positive value of second virial coefficient shows that solute-solvent interaction is high leading to stable suspension. The results of this work are a clear indication that U(IV) hydrolysis does not differ from hydrolysis of Pu(IV).

1. Introduction

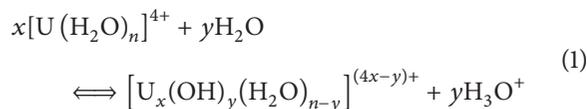
Due to high electric charge, tetravalent actinides have an inordinate tendency to undergo hydrolysis leading to formation of polynuclear species of colloidal dimensions even under very acidic conditions [1–4]. Such processes are observed for tetravalent ions such as Th(IV), Pu(IV), U(IV), Np(IV), and Pa(IV), and to a lesser extent for the hexavalent actinyl ions U(VI) and Pu(VI) [5–7]. The initial step in hydrolysis is the formation of mononuclear species. But further hydrolysis may lead to a variety of polynuclear species [8, 9]. Consider, for example, above millimolar concentration and close to the solubility limit, Pu(IV) form polynuclear species [10]. The consequences of formation of polynuclear species include excessive foaming in evaporation operation, clog in transfer lines, interference in ion exchange operations, and emulsification in solvent extraction operations, and mainly it can lead to criticality hazard due to increase in local concentration of Pu [11]. Colloids can also facilitate the transport of actinide elements in the environment. The transport of plutonium from repository to surrounding may increase when the stable colloidal Pu(IV) formed in ground water comes in contact with spent nuclear fuel [12]. Rate of mobility depends on

the size of colloids. For instance, colloids of smaller size less than 50 nm have high mobility and surface to volume ratio [13, 14]. Similarly the nature of colloidal polymers also plays a significant role. Freshly formed colloidal polymers dissolve easily upon dilution or by acidification. But ageing of polymers leads to structural transformation from hydroxide bonds to oxygen bonds and in other words the polymer becomes insoluble making it more difficult to depolymerize [15].

In order to avoid the formation of polymers and to determine the possible role of colloids as carrier of activity from a nuclear waste vault, it is important to understand the mechanism of colloid formation. Hence some of the actinides such as U(IV), Th(IV), and Zr(IV) due to their similarity in hydrolysis behavior and colloid chemistry of Pu(IV) have been chosen as analogue in order to have insights into aqueous chemistry of Pu(IV) [16]. It is easier to perform investigation on these elements, due to their nonradioactivity, weaker hydrolyzing nature, and ease in handling.

In the present study, U(IV) has been chosen although U(VI) is the most common species in the environment. U(IV) is also considered as toxic waste under strongly reducing conditions that is often accepted to be present in deep geological repositories [17]. The solubility of U(IV) is

less than U(VI) by many orders of magnitude. But under certain conditions it forms stable colloids which lead to its mobilization. U^{4+} exists as $[U(OH)_x]^{(4-x)+}$ in solution due to hydrolysis [18]. The hydrolysis reaction of U(IV) resulting in the formation of polynuclear hydrolysis complexes is given in the following:



There are a considerable number of studies on U(IV) hydrolysis and polymerization [19, 20]. Laser-induced breakdown detection measurements show that precipitation from higher concentrated solutions with respect to uranium leads to small particles of $dP \sim 10$ nm at pH around 1. Solutions with low uranium content give larger particles of roughly 100 nm at pH around 3. U(IV) hydrolysis is not solely of interest due to its existence only at highly acidic conditions [21]. But if the required conditions are met, the results will be significant in order to compare with Pu which cannot be handled directly.

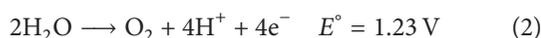
Colloids can be characterized by many techniques such as transmission electron microscopy, scanning electron microscopy. But they are destructive and rather time-consuming sample preparation has to be performed. Hence it is not possible to study aquatic colloids in their natural surroundings. In the present work, light scattering method is used as it is nondestructive, noninvasive and can even be applied to dilute suspensions of small particles without sample preparation [22]. In addition to that, molecular weight of the polymers formed due to accidental dilution during fuel processing can also be determined by this technique.

2. Experimental Section

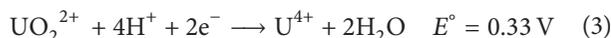
2.1. Materials

2.1.1. Aqueous U(IV) Solutions. Feed uranyl solution was prepared by dissolving U_3O_8 powder by using 1–1.5 M HNO_3 (M/S Fisher, assay of 69–71% w/w). Feed solution is subjected to electrolysis by proper dilution. The electrolytic setup consists of a platinum anode and titanium cathode. 0.5–1 M HNO_3 is used as anolyte and 100–150 g per litre of uranyl as catholyte. 0.5 M hydrazine is added in order to avoid oxidation of U(IV) to U(VI). The reactions taking place at the cathode and anode are given in the following:

Anode



Cathode



2.2. Colloid Synthesis. U(IV) solution of different concentration of 0.4 mM to 19 mM was prepared by diluting the solution with millipore water. Water used for making the

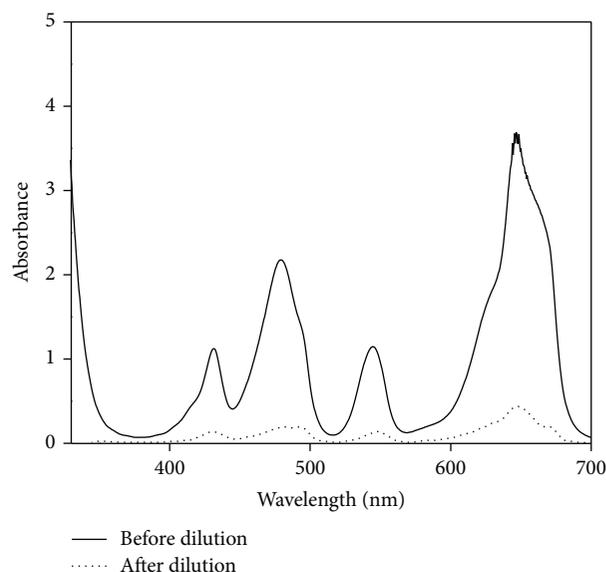


FIGURE 1: UV-Vis spectra of U(IV) solution in the course of its dilution.

solutions was ASTM grade I water with a resistivity of $18.2 \text{ M}\Omega\text{-cm}^{-1}$ at 298.15 K and TOC < 15 ppb, obtained from a Millipore simplicity system. pH of the solution was adjusted by gradually adding 0.1 M NaOH (M/S Merck, AR grade).

2.3. Measurement of pH and Refractive Index. The changes in the pH of the solutions were monitored using Thermo scientific Orion 3-star bench top pH meter. The glass electrode used for the measurement was calibrated with buffer solutions of pH 4.01 and 7.00. The accuracy of pH measurements was ± 0.01 units. Refractive index (n_D) of solutions of different concentration of U(IV) was measured on Anton Paar RXA 156 refractometer equipped with integrated peltier thermostat with standard deviation of $2 \times 10^{-5} n_D$ at 298 K.

2.4. UV-Visible Electronic Absorption Spectra. UV-visible electronic absorption spectra were recorded with a Shimadzu UV-visible-NIR 3600 spectrophotometer. The instrument was equipped with photomultiplier tube for the ultraviolet and visible regions. It uses a high-performance double monochromator which makes it possible to attain an ultralow stray-light level (0.00005% max. at 340 nm) with a high resolution. The maximum spectral resolution was 0.1 nm. Absorption spectra were recorded between 300 and 700 nm with an accuracy of 0.1 nm.

2.5. FTIR Spectra. FTIR spectra were recorded using a Fourier transform IR ABB MB3000 spectrometer equipped with DTGS detector and an ATR attachment. The interferometer was equipped with a nonhygroscopic-ZnSe beam splitter. All the spectra were measured at a spectral resolution of 4 cm^{-1} and 100 scans were taken per sample. The frequency accuracy was $< 0.06 \text{ cm}^{-1}$. Solutions were placed on the crystal. Millipore water was used as reference to minimize signal from water peaks during data collection.

TABLE 1: Concentration of U(IV) and pH at the onset of colloid formation, intensity average size (d_{50}), and pH at maximum colloid formation.

[U(IV)] in mM	pH at initial colloid formation	d_{50} in nm	pH at maximum colloid formation
0.4202	Colloids not observed	—	—
1.2605	Colloids not observed	—	—
2.5210	3.46	20.59	—
3.7815	2.85	15.12	4.25
5.2100	2.74	15.46	4.20
6.5126	2.67	10.37	4.17
7.8151	2.52	10.02	3.30
9.1176	2.44	10.60	3.03
13.0	2.10	4.31	2.51
19.0	1.84	5.16	1.95

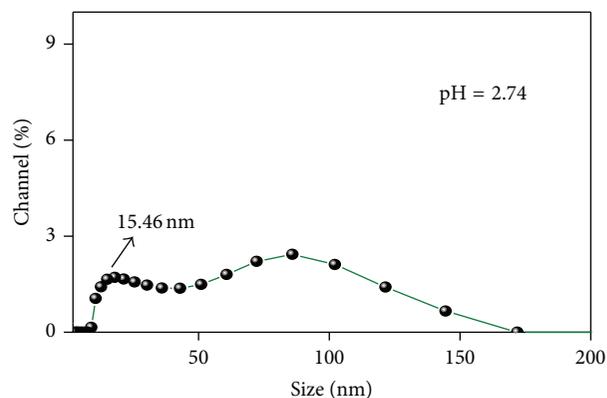
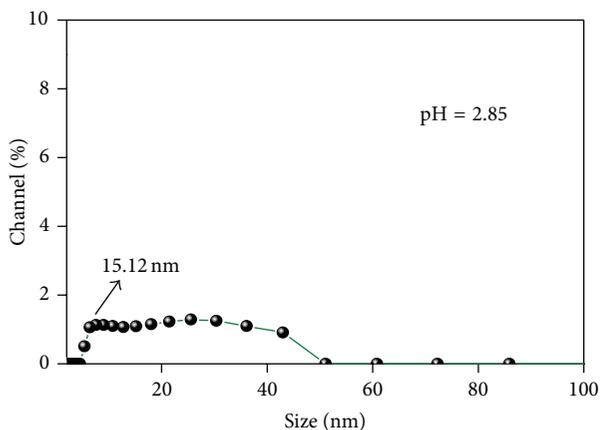
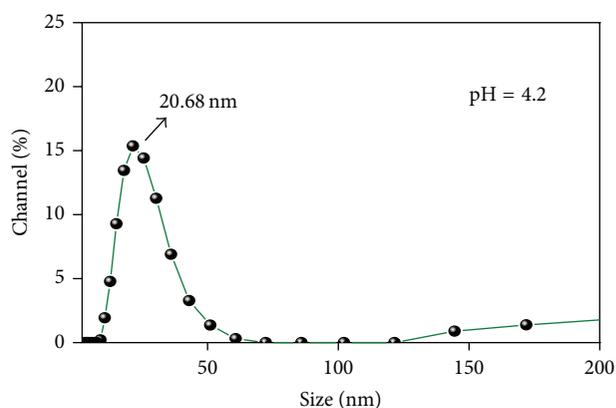
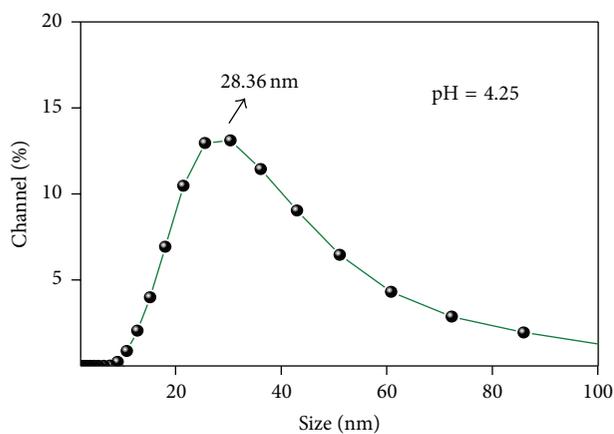


FIGURE 2: Intensity averaged particle diameter (d_{50}) of U(IV) hydrolyzed colloid formed in 3.78 mM solution diluted to different pH.

FIGURE 3: Intensity averaged particle diameter (d_{50}) of U(IV) hydrolyzed colloid formed in 5.2 mM solution diluted to different pH.

2.6. Light Scattering Measurements. Both SLS and DLS experiments were performed using Microtrac (Nanotracs ULTRA) particle size analyzer. The light source was a 780 nm, 3 mW diode laser. The scattered light was measured at an angle of 180° . Scattering experiments were performed at a temperature of $27 \pm 1^\circ\text{C}$. The performance of the instrument was checked with the reference material (100 nm polystyrene microsphere

suspended in water) prior to particle size measurements. 50 scans were taken for each sample. The uncertainty in the measurement was found to be ± 1 nm. It uses a unique method called the controlled reference method, where the scattered light beats against a stable reference, that is, the laser source itself. The scattered light from the particle and the reference (reflected laser) interferes at the detector. The signal is modulated by Brownian diffusion of particles. It was

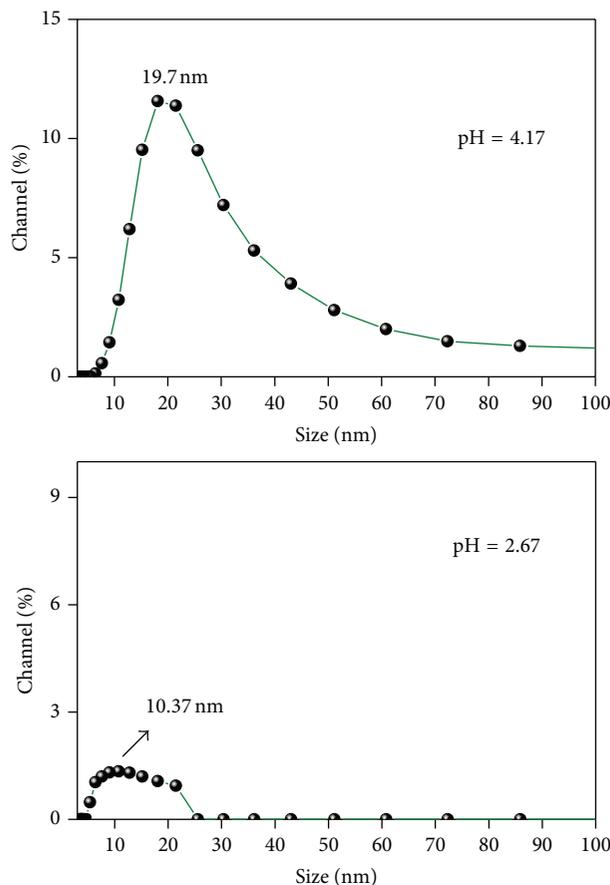


FIGURE 4: Intensity averaged particle diameter (d_{50}) of U(IV) hydrolyzed colloid formed in 6.5 mM solution diluted to different pH.

transformed by fast Fourier into power spectrum from where the size distribution is derived.

3. Results and Discussion

3.1. Particle Size. Before proceeding with the experiments, it was ensured that there was no oxidation after dilution and U(IV) species are stable at the present condition by taking a blank run in UV-Vis spectrophotometer as it can be used to detect higher concentration of U(IV) of the order of 5×10^{-5} M. Figure 1 shows the UV-Vis spectra taken for the stock solution and diluted solution with a total uranium concentration of 0.4 mM. There was no considerable change in the spectrum of diluted U(IV) solution, and hence it was confirmed that the maximum species present are U(IV).

A series of U(IV) solutions was measured by light scattering with concentrations of 0.4 mM–19 mM. For each series, the pH was varied, starting at pH 1 and increasing to pH 4 obtained by adding 0.1 M sodium hydroxide (Table 1).

(i) 0.4–2.5 mM U(IV) Solutions. In case of 0.4–2.5 mM U(IV) solutions when the pH of the solution is increased and light scattering measurements are made every 0.2 units until pH 3, there is no significant difference from the starting solution which shows that these solutions are considered to be colloid free. At pH beyond 4 there are only particles greater

than 1000 nm which is considered to be the amorphous precipitates that has been formed.

(ii) 3–7 mM U(IV) Solutions. The solution darkens when pH is increased consistent with the presence of colloidal U(IV) [23]. The particle refractive index was assumed as 1.95 to obtain the size distribution [24]. The intensity distribution curves for colloidal 3.78 mM U(IV) solution at different pH are shown in Figure 2. The initial colloid formation starts at pH 2.85 and the size of the colloids initially formed is found to be 15.12 nm. When pH is increased to 4.25, the mean colloid size increases to 28.36 nm and the colloid content is even higher which could be observed from the volume of the distribution curve. The increase in size is due to the addition of OH^- or H_2O ligands to the growing structural network. A combined LIBD and UV-Vis studies carried out on Pu(IV) hydrolysis products proved that the colloid formation is preceded by formation of small polynuclear species <5 nm and colloids larger than 5 nm are formed with increasing pH [25]. The volume of peak for initially formed colloids is small in all cases irrespective of concentration. Similar results were observed for 4–7 mM U(IV) solutions. Figures 3 and 4 show the intensity size distribution for 5.2–6.5 mM U(IV) with varying pH. The colloids formed at these concentrations were found to be stable for longer time and there was no much variation in particle size with increasing pH.

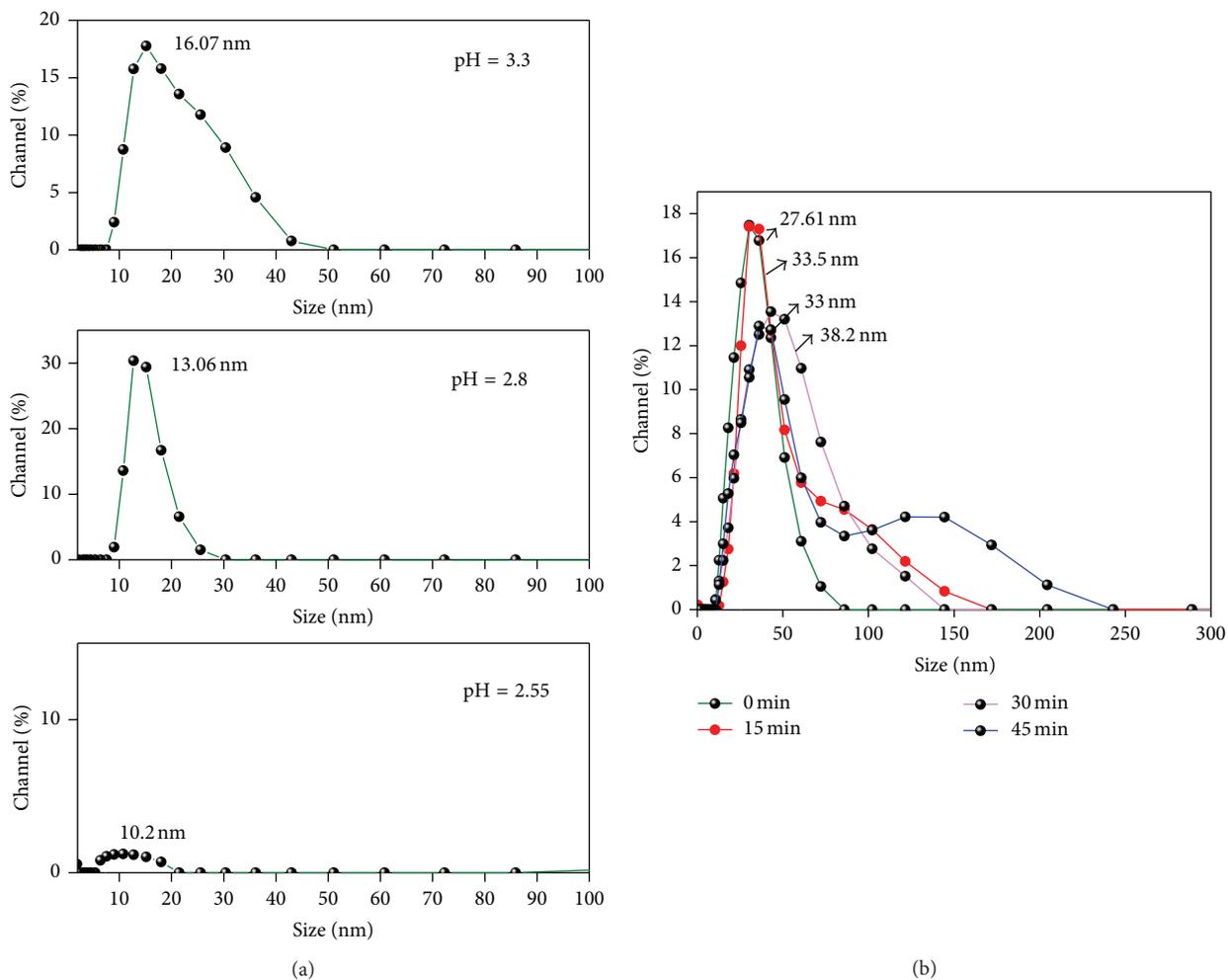


FIGURE 5: (a) Intensity averaged particle diameter (d_{50}) of U(IV) hydrolyzed colloid formed in 7.8 mM solution diluted to different pH. (b) Variation of particle size with time at the point of precipitation for 7.8 mM U(IV) solution at pH 3.65.

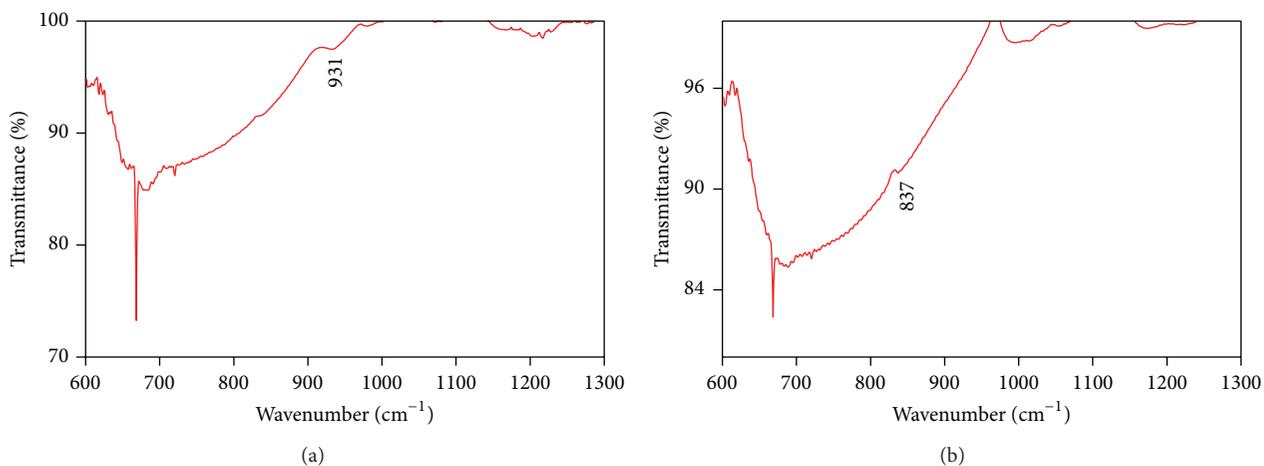


FIGURE 6: (a) FT-IR ATR spectra of [U(IV)] = 19 mM diluted to pH 1. (b) [U(VI)] = 2.52 mM diluted to pH 3.46.

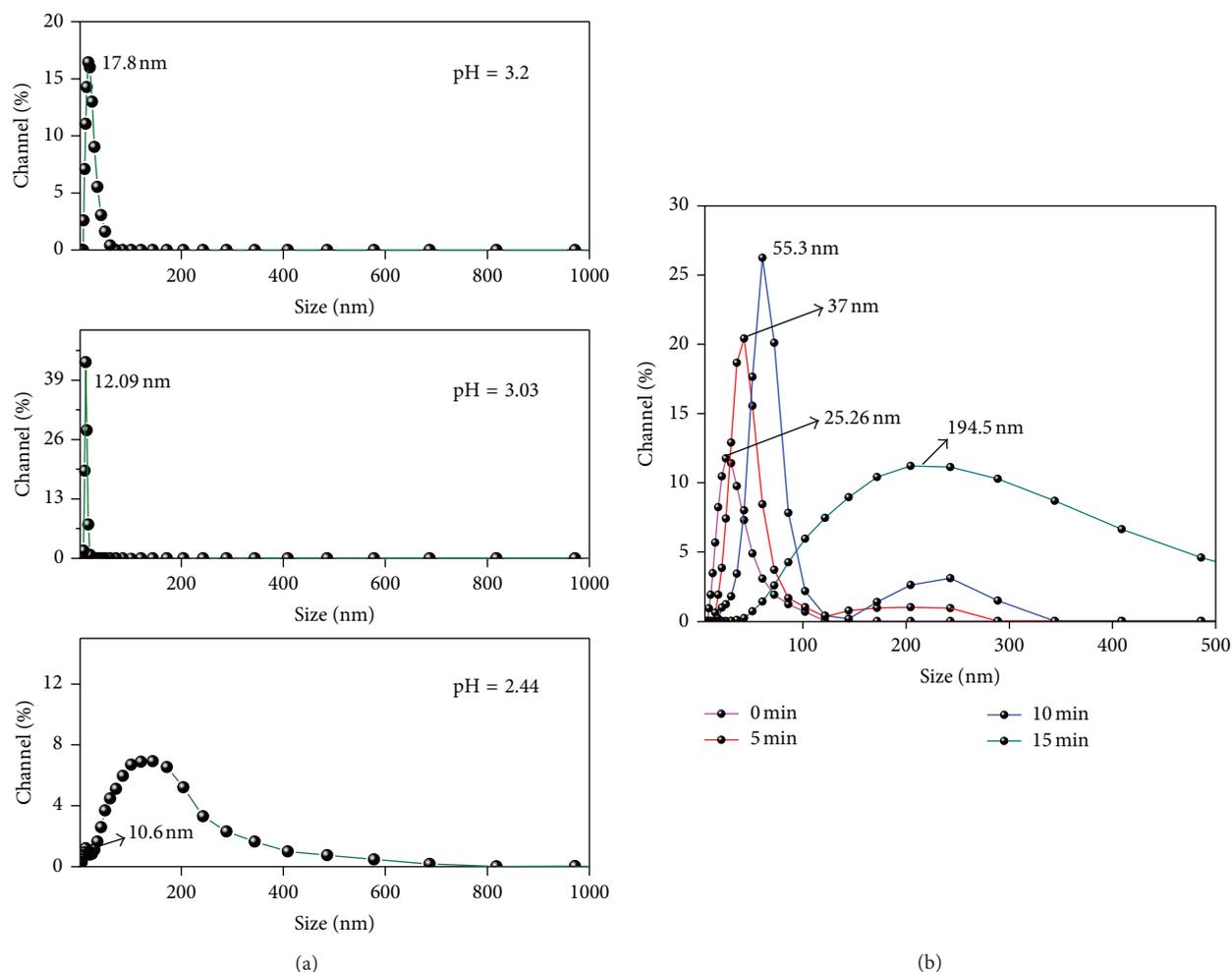


FIGURE 7: (a) Intensity averaged particle diameter (d_{50}) of U(IV) hydrolyzed colloid formed in 9.2 mM solution diluted to different pH. (b) Variation of particle size with time at the point of precipitation for 9.2 mM U(IV) solution at pH 3.3.

(iii) 7.8–19 mM U(IV) Solutions. When the concentration is increased to 7.8 mM, there is further decrease in size of colloids initially formed. This is mainly due to crystalline nature of colloids formed at higher concentration [21]. Figure 5(a) shows the size variation of 7.8 mM U(IV) solutions at different pH and Figure 5(b) shows the variation of particle size with time at the point of precipitation. Figures 6(a) and 6(b) show the FTIR spectra for 19 mM diluted to pH 1.8 and 2.52 mM diluted to pH 3.46. It shows a band at 931 cm^{-1} due to U–O stretching which is not seen in 0.4 mM U(IV). It ensures the presence of UO moiety which makes the colloids more crystalline [26]. When pH of the solution is further increased, the colloid suspension starts precipitating and the size variation at the point of precipitation at different time intervals clearly shows that the colloidal species aggregates to particles of bigger size. Bimodal distribution appeared 45 min after the sample preparation due to very fast particle aggregation. This behavior is similar to Pu(IV) colloids that has been formed in low acid medium. Its size varies from a few nanometers to almost micrometers depending on the conditions of generation. SANS (small angle neutron scattering) measurements on Pu polymer show that the size

ranges from 10 \AA to 1000 \AA [27]. The above results show the similarity in hydrolytic behavior of U(IV) with Pu(IV). Similar trend is observed when concentration of U(IV) is increased. But in case of higher concentration, there is drastic change in particle size within short interval of time. This is due to increase in degree of polymerization at higher concentration. Figures 7(a), 8(a), and 9(a) show the size variation of 9.2–19 mM U(IV) solutions at different pH and Figures 7(b), 8(b), and 9(b) show the variation of particle size with time at the point of precipitation at a particular pH. As concentration increases, the corresponding pH at the point of precipitation decreases.

The change in refractive index with concentration has been plotted. The differential refractive index has a positive slope. The refractive index increases with increase in the concentration of the solute. The dn/dc value is determined as 0.0927 g mL^{-1} . This value is used for generating the Debye plot. Figure 10 shows the refractive index variation with concentration of U(IV).

3.2. Molecular Weight. The extent of polymerization in case of Pu is found to vary from 10 to 10^8 molecular units. The

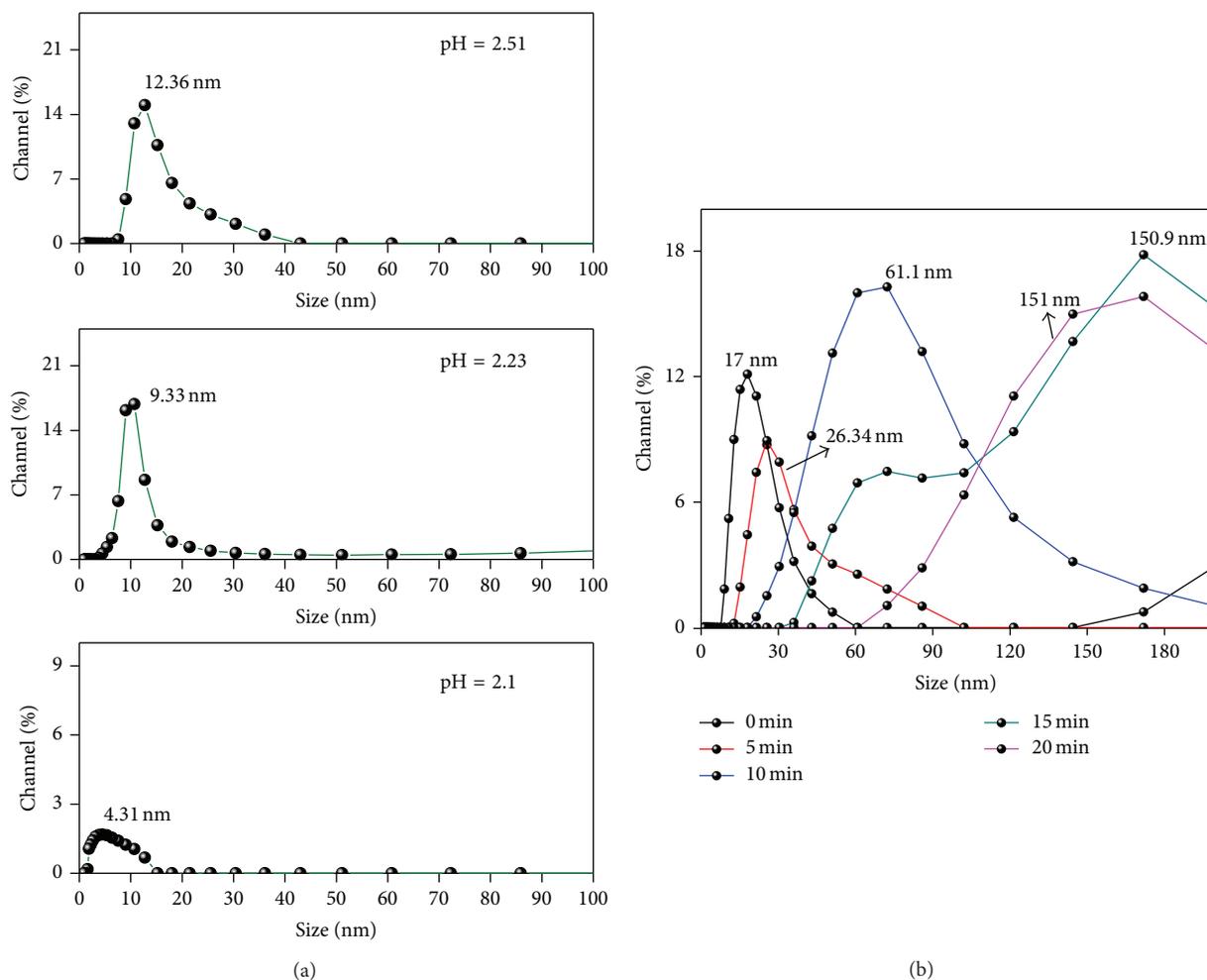


FIGURE 8: (a) Intensity averaged particle diameter (d_{50}) of U(IV) hydrolyzed colloid formed in 13 mM solution diluted to different pH. (b) Variation of particle size with time at the point of precipitation for 13 mM U(IV) solution at pH 2.61.

TABLE 2: Calculated parameters from the Debye plot.

Substance	Ageing time (days)	Measured at $\lambda = 780$ nm	
		M_w (Da)	Second virial coefficient, A_2 (Mlg $^{-1}$ Da)
U(IV) hydrolyzed polymer	Fresh colloid	1,820	4.96×10^{-1}
	1	4,630	8.68×10^{-3}
	3	13,000	2.54×10^{-2}

molecular weight of the freshly formed Pu polymer has been reported as 4.2×10^5 Da by diffusion studies and 2×10^7 by ultracentrifugation [28]. The variation is possibly due to the method of preparation. But in general it was widely accepted that the molecular weight of freshly formed Pu(IV) colloidal polymer is 4,000 Da and it reaches a maximum of 10^{10} Da when aged [29, 30]. The molecular weight of polymers formed can be measured by Debye plot if the particle size is much smaller than the wavelength of the incident light. Since the particle size of U(IV) colloids formed is very small, an attempt was made to determine the molecular weight. All the particles are assumed to be spherical. Our present study reveals that the molecular weight of U(IV) polymer when measured immediately after preparation has a value

of 1,800 Da. When aged for around 1 day, it increases to 4,000 Da. At the end of third day it reached a maximum of 13,000 Da. This is in good agreement with the behavior of Pu(IV) polymer as the molecular weight increases with ageing. Recently, authors have already reported the molecular weight of freshly formed Zr(IV) and U(VI) polymers [31, 32]. U(IV) behaves comparatively similar to Zr(IV) but differs from that of U(VI) whose molecular weight does not change upon ageing. The size of the polymeric colloid was ~ 10 nm when freshly prepared and at the end of the third day it was 44 nm. This is due to addition of many monomeric units to the polymer. From the calculated molecular weight it has been predicted that ~ 15 atoms of U are present in the polymeric unit at the initial stage and increase to ~ 50 atoms

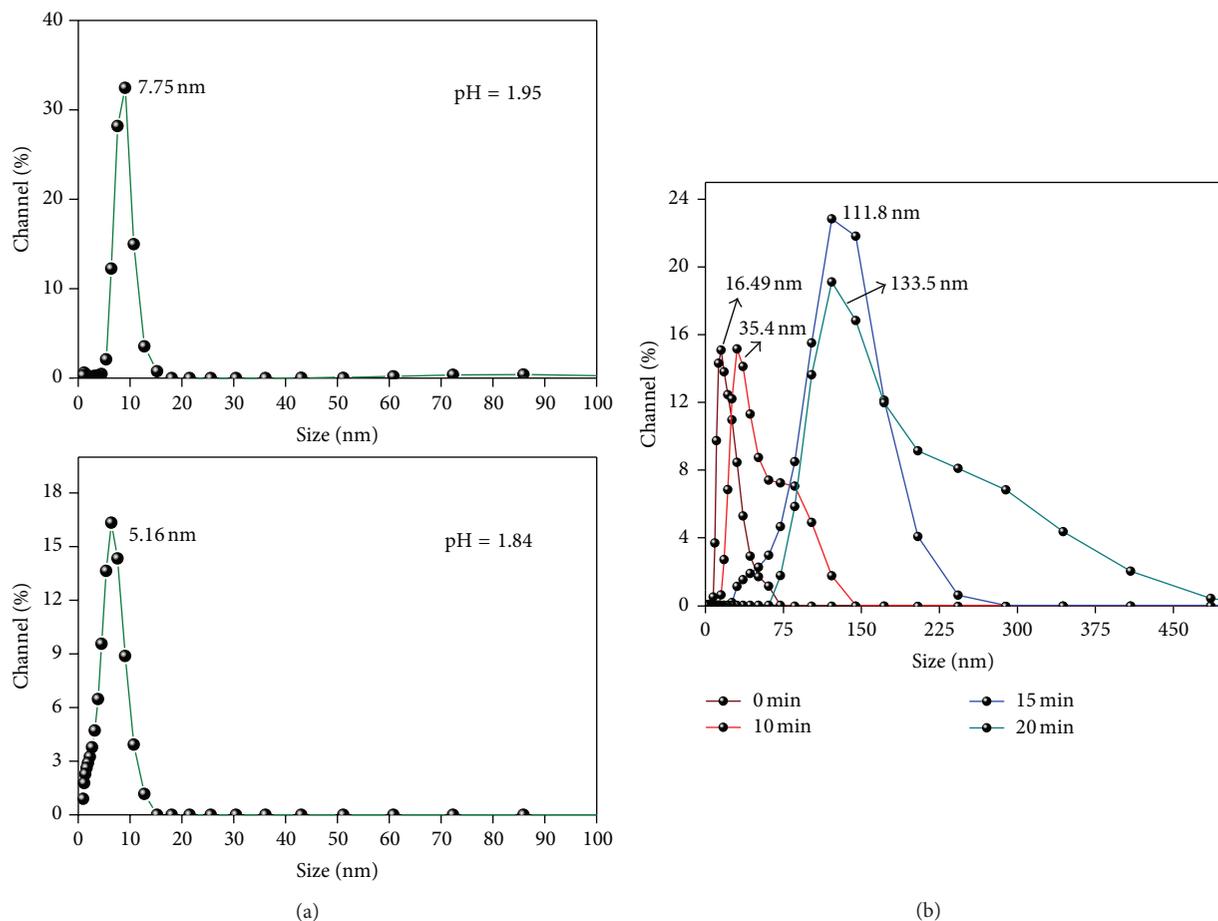


FIGURE 9: (a) Intensity averaged particle diameter (d_{50}) of U(IV) hydrolyzed colloid formed in 19 mM solution diluted to different pH. (b) Variation of particle size with time at the point of precipitation for 19 mM U(IV) solution at pH 2.42.

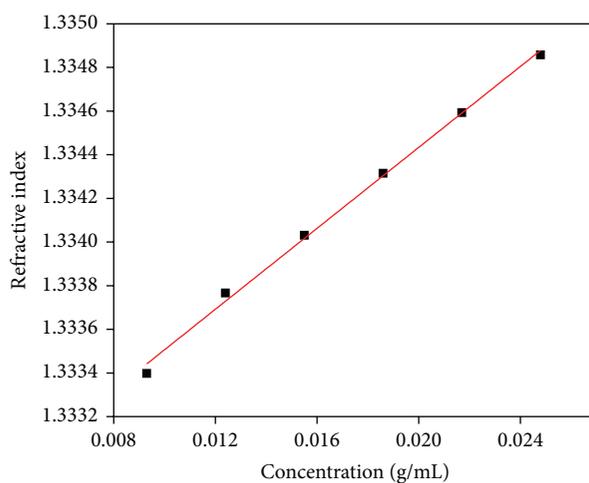


FIGURE 10: The dn/dc curves obtained for different concentration of U(IV) solution ($R^2 = 0.9965$).

with increase in time. As all the experiments were done at open atmosphere, ageing beyond three days was difficult as U(IV) gets oxidized to U(VI).

The nature of solute-solvent interaction existing in the solution can be determined by evaluating the second virial

coefficient. The slope of the Debye plot gave a positive value. It shows that the colloidal U(IV) suspension is stable due to higher solute-solvent interaction. The molecular weight (M_w) and A_2 values are tabulated in Table 2 at different ageing time. Figure 11 shows the Debye plot for uranyl

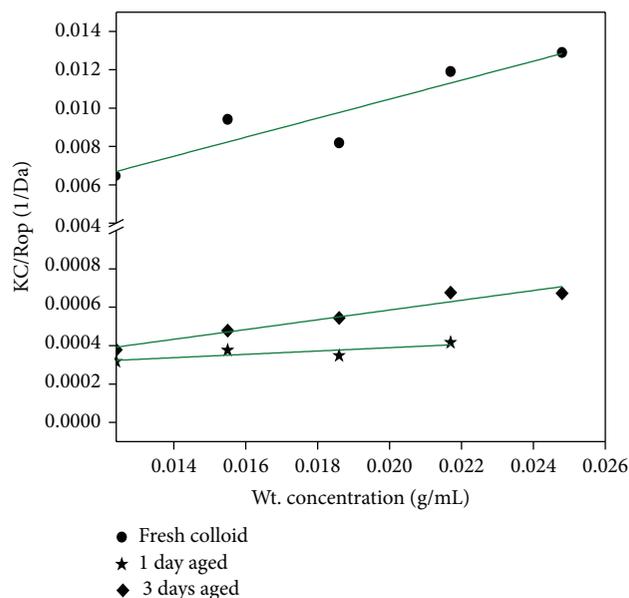


FIGURE 11: Debye plot of U(IV) polymeric solution aged at different time intervals.

(VI) colloidal polymers aged at different time intervals. The calculated parameters from the Debye plot such as weight average molecular weight for freshly prepared and aged U(IV) hydrolyzed polymer, second virial coefficient are summarized in Table 2.

4. Conclusions

Solutions of tetravalent U at concentrations between 0.4 and 19 mM ($1 < \text{pHc} < 4$) are investigated by light scattering. It has been confirmed that the colloidal particles initially formed at higher concentration are smaller than those formed at lower concentration. Colloids formed at lower concentration are found to be more stable than colloids formed at higher concentration. The obtained molecular weight of the colloidal polymers aged at different time intervals clearly indicates the similarity in hydrolytic behavior of U(IV) with Pu(IV). The molecular weight of U(IV) hydrolyzed polymer has also been reported.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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