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Effects of Hypochlorite Ion on the Solubility of Amorphous Schoepite at 25 °C in Neutral to Alkaline Aqueous Solutions

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*Solubility / Uranyl hydroxide (Schoepite) /
Effect of hypochlorite ion*

Abstract

Solubilities of schoepite with hypochlorite ion in 0.1 M NaCl solution were measured by potentiometric titration method at 25.0 °C, under CO₂-free atmosphere. Compared with its solubility in the absence of hypochlorite ion, it has been found that hypochlorite ion enhanced its solubility up to 100 times in the neutral pH range. The appearance of a shoulder at 311 nm in UV-Vis spectra indicated the presence of a new chemical species, which might affect on the solubility of schoepite in solution. Furthermore, changes in its solubility at pH 8.3 and in the vibrational frequency (ν_3) for asymmetric stretching mode of U–O double bond at different molar ratios of hypochlorite ion to uranyl ion concentration provided an experimental evidence that a new chemical species was formed with hypochlorite ion. X-ray diffraction patterns for the residual precipitates also showed three different diffraction angles, which is resulted from the introduction of hypochlorite ion in precipitates.

Introduction

For the safety assessment of nuclear waste disposal, it is necessary to understand the chemical interaction of radionuclides in groundwater or surface water for their migration behavior in geological media. For the prediction of migration behavior using geochemical or thermodynamic models, solubility limits would be a primary parameter to be determined from stability constants for a number of chemical species in solution. In a previous report on solubilities of americium hydroxide, Am(OH)₃, hypochlorite ion (OCl⁻) was found to be formed by a strong alpha-radiolysis in chloride media, and the increase in its solubility was due to changes in its oxidation state to AmO₂⁺ [1]. There was an indication of the formation of PuO₂²⁺–OCl⁻ complex in another report [2]. Both its strong oxidizing ability and the complexation of hypochlorite ion with actinide dioxo-cation could affect on the solubility and the dissolution behavior of actinide hydroxo-compounds.

Studies of the chemical behavior of uranium have played important roles in the treatment of spent fuel matrix and of radioactive waste. It was found that Schoepite, UO₂(OH)₂ · H₂O(s) (chemically equivalent to UO₃ · 2H₂O), equilibrated with uranyl hydroxo complex, (UO₂)₃(OH)₅⁺ [3]. As plutonium(VI), uranium(VI) is the sole oxidation state with hypochlorite

ion in neutral to alkaline pH range in aqueous NaCl solution [2, 4]. In this paper, solubilities of schoepite with hypochlorite ion were measured in 0.1 M NaCl solution under CO₂-free environment, and the results compared with measurements in the absence of hypochlorite ion under the same condition. Formation of new chemical species in solution were investigated with UV-Vis and FT-IR spectrophotometer, and could be explained with changes in the solubility of schoepite at a fixed pH value for different molar ratios of hypochlorite ion in solution. Changes in diffraction patterns for the residual precipitates equilibrated with solution were observed by X-ray diffraction analysis.

Experimental

Chemicals

Uranium(VI) peroxide was precipitated by adding a small volume of 30% hydrogen peroxide to uranium(VI) perchloric acid solution at pH 2 adjusted with concentrated ammonia solution [5]. Uranium(VI) chloride acid solution was prepared by dissolving uranium(VI) peroxide precipitates in 1.0 M HCl and evaporating the residual hydrogen peroxide in solution. Uranium concentration in stock solution was 0.7246 M, which was determined by titration with potassium dichromate solution [6]. Fresh NaOCl solution (Aldrich Chemical Co., 5% Cl⁻) was used in the experiment. Its concentration determined by iodometry with a standard Na₂S₂O₃ solution [6] was 0.4997 M, and its molar extinction coefficient at 291.0 nm was 365.0 ± 2.0 M⁻¹ cm⁻¹. Other chemical reagents including sodium chloride (Merck, pro-analyti) were used with no additional purification. Double-distilled demineralized water passed through Milli-Q Reagent Water System (Millipore Co.) was boiled and cooled in a nitrogen gas bubbling to get rid of dissolved carbon dioxide in water.

Procedure

All the experiments for the solubility measurement were carried out under a CO₂-free atmosphere. In order to have the solubility data of uranium(VI) hydroxide (schoepite) at various pH values, two water-jacketed potentiometric titration vessels were mounted

Table 1. Solubilities of schoepite at different pH values in the solution with OCl^- and without OCl^-

No.	Solubility with OCl^-		Solubility without OCl^-	
	pH	$[\text{U(VI)}]_{\text{soln.}} (\times 10^6 \text{ M})$	pH	$[\text{U(VI)}]_{\text{soln.}} (\times 10^7 \text{ M})$
1	9.84	1.94	9.84	5.14
2	9.33	1.88	9.17	2.19
3	9.10	1.74	9.08	4.24
4	8.45	2.14	8.87	1.93
5	8.42	2.18	—	—
6	8.34	1.92	—	—
7	8.27	2.33	—	—
8	8.18	2.32	8.15	1.66
9	8.05	2.05	—	—
10	7.88	2.30	7.67	0.602
11	7.42	2.80	7.43	0.387
12	7.29	2.15	—	—
13	7.14	1.82	—	—
14	7.00	1.97	6.97	0.505
15	6.88	2.26	6.72	0.278
16	6.59	2.73	6.62	0.165
17	6.59	2.54	6.40	0.180
18	6.23	4.13	—	—
19	5.26	10.4	5.89	0.747

* Molar extinction coefficient of uranyl-arsenazo(III) complex at 655 nm was $3.387 \times 10^4 / \text{M cm}$.

in a CO_2 -free atmosphere (glove box). Temperature was maintained at $25.0 \pm 0.1^\circ \text{C}$ with a circulating water bath (Haake-Buchler Model A81). Initially, a few hundreds microliter of diluted uranyl ion stock solution were introduced into both titration vessels with 100 ml of 0.1 M NaCl solution, having uranyl ion concentration of $0.789 \times 10^{-4} \text{ M}$ in solution. To raise its pH value at pH 9.5, several hundreds microliter of CO_2 -free 0.1 M sodium hydroxide solution were added in solution. Stirring for overnight, uranyl hydroxide (schoepite) was formed in both titration vessels. Adding a small volume of hypochlorite stock solution into one of the titration vessels, hypochlorite ion concentration was $9.824 \times 10^{-4} \text{ M}$ in solution. Whenever the solution was disturbed, it was stirred for 3 days, and let it stand for a day. According to our preliminary test, the first steady state for the solubility measurement was achieved at a fixed pH after 4 days. Solubility measurements should be made at an equilibrium between the solution and the solid phase. However, it took so long time that the aliquot was taken at the first steady state. After reaching equilibrium (actually, "steady state"), the pH value in solution was recorded. About a 2 ml aliquot was taken from the titration vessel at that pH value, and the solution adjusted to a new pH value with several drops of 0.1 M HCl or CO_2 -free 0.1 M NaOH solution. The aliquot was filtered with 450 nm disc filter (Millex HA, 25 mm diameter, Millipore Co.). A small portion of filtered aliquot was used for recording the UV-Vis spectra in UV-Vis spectrophotometer (Varian Techtron Pty Ltd., Cary 5) and the other portion was used for the determination of the total uranium concentration in solution from the ab-

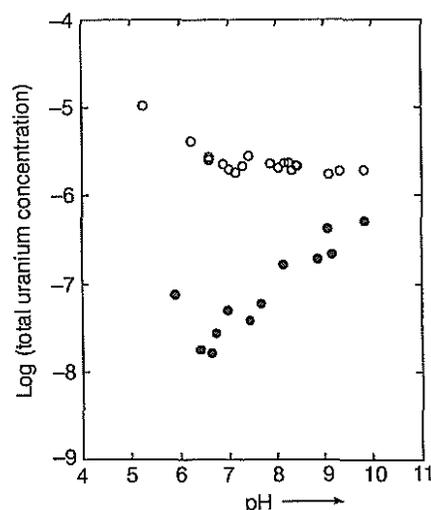


Fig. 1. Solubilities of uranyl hydroxide (schoepite) with hypochlorite ion (O) and without hypochlorite ion (●) in 0.1 M NaCl solution. $[\text{UO}_2^{2+}]_0 = 9.789 \times 10^{-4} \text{ M}$, $[\text{ClO}^-]_0 = 9.824 \times 10^{-4} \text{ M}$.

sorbance of the uranyl-arsenazo(III) complex at 655.0 nm in the UV-Vis spectrophotometer.

For batch experiments, the solubility of uranyl hydroxide (schoepite) was measured at fixed pH value with different molar ratios of hypochlorite ion in solution. Total uranium concentration in solution was determined by either a laser fluorescence uranium analyzer (K.A.E.R.I. Model UA-100) using Fluran (Scintrex), or ICP atomic emission spectrometer (ISA Jobin-Yvon JY 50 P). Under the same condition, FT-IR spectra for monitoring changes in chemical species of each solution were recorded with a Zn-Se circle cell in FT-IR spectrometer (Bomem Model IMH 4800L).

After the solubility measurements, the residual precipitates in both titration vessels were investigated by X-ray diffraction analysis (Siemens D 5000 Diffractometer).

Results

The measured solubilities of schoepite in 0.1 M NaCl and in the same solution with hypochlorite ion in neutral to alkaline pH range are listed in Table 1. As shown in Figure 1, solubilities of schoepite in 0.1 M NaCl solution increased from the range of 10^{-8} M to 10^{-7} M with their pH values, and those with OCl^- in the same solution were $2 \times 10^{-6} \text{ M}$ to $3 \times 10^{-6} \text{ M}$ in the range of pH 6.0 to 9.8. The presence of hypochlorite ion in solution enhanced its solubility up to 100 times greater than one measured without hypochlorite ion in neutral pH range. Along with the solubility measurements, typical UV-Vis spectra for the solution phase at different pH values were recorded, as shown in Figure 2. The shoulder at 311 nm for solutions with hypochlorite ion appeared in a whole pH range.

UV-Vis spectra for the hydrolysis products of uranyl ion in solution were reported earlier [7]. It is am-

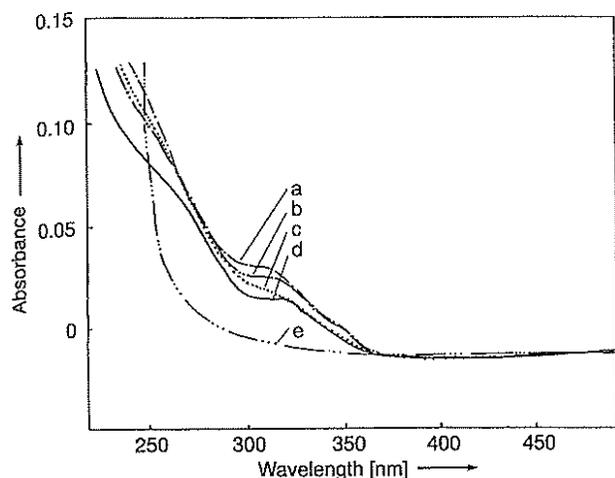


Fig. 2. UV-Vis spectra for solution phase at different pH values in the presence of OCl^- ion and for solution phase at pH 7.85 without OCl^- ion. (a) pH 6.59, (b) pH 7.42, (c) pH 8.45, (d) pH 9.33, and (e) no hypochlorite ion.

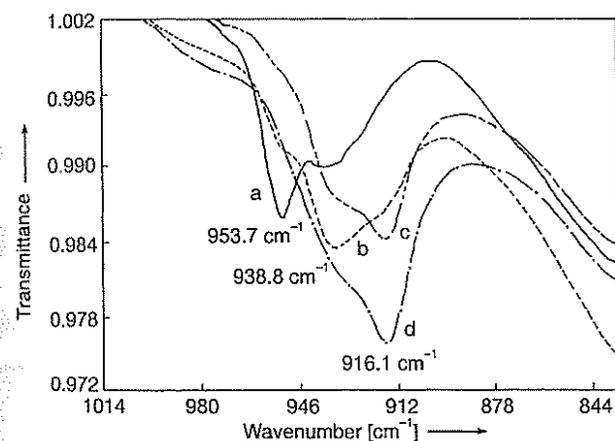


Fig. 3. FT-IR spectra for uranyl ion in D_2O solution at different pH values. $[\text{UO}_2^{2+}]_0 = 5.05 \times 10^{-3} \text{ M}$; (a) pH 3.2, (b) pH 4.1, (c) pH 4.5, and (d) pH 5.3.

ambiguous to use their spectra for the chemical speciation of uranyl ion in complexation, because of their broad band-width. However, FT-IR spectra of uranyl ion in D_2O solution at different pH values obtained in this experiment clearly showed changes in vibrational frequency, corresponding to the ν_3 asymmetric stretching mode of U–O double bonds in uranyl dioxo-cation. As shown in Figure 3, vibration frequencies for UO_2^{2+} , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and $(\text{UO}_2)_3(\text{OH})_5^+$ in FT-IR spectra were 953.7 cm^{-1} , 938.8 cm^{-1} , and 916.1 cm^{-1} , respectively. Absorption band for free OCl^- appeared at 915.5 cm^{-1} in the spectrum. In Figure 4, FT-IR spectra were recorded for uranyl solutions with different molar ratios of hypochlorite ion concentration to initial uranyl ion concentration at a fixed pH value (pH 5.0). A new absorption band appeared at 933 cm^{-1} grew with hypochlorite ion concentration to its molar ratio of 0.13, however, its absorption intensity was reduced at molar ratios higher than 0.2. The absorption band at 933 cm^{-1} slowly disappeared with the growth of a new

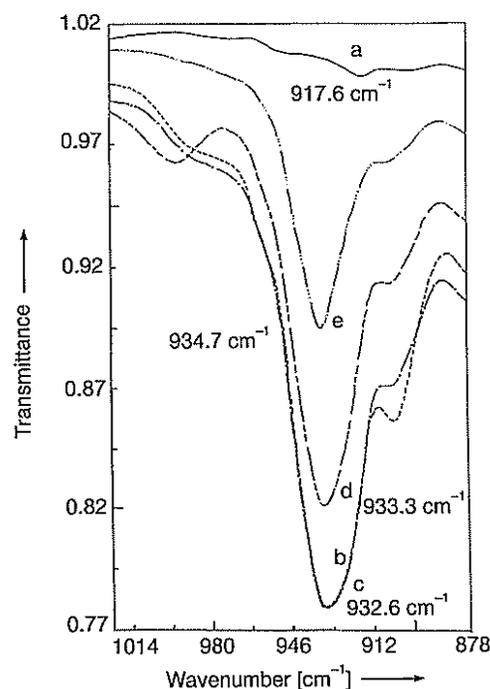


Fig. 4. FT-IR spectra for uranyl ion with OCl^- at different molar ratio in D_2O solution. $[\text{UO}_2^{2+}]_0 = 5.05 \times 10^{-3} \text{ M}$; (a) 1:0.07 (pH 5.07), (b) 1:0.13 (pH 5.00), (c) 1:0.20 (pH 5.04), (d) 1:0.27 (pH 4.95), (e) 1:0.33 (pH 4.96).

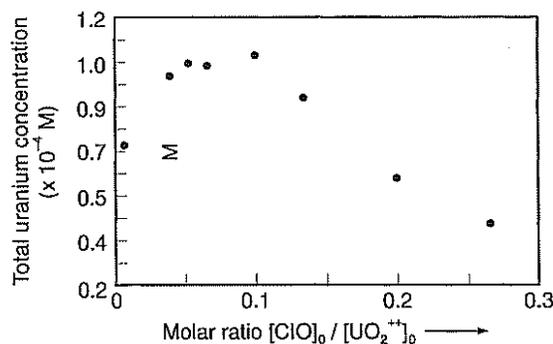


Fig. 5. Solubilities of uranyl hydroxide (schoepite) for different molar ratios of hypochlorite ion concentration to initial uranyl ion concentration in 0.1 M NaCl solution at pH 8.3, and $[\text{UO}_2^{2+}]_0 = 9.789 \times 10^{-4} \text{ M}$.

absorption band at 948 cm^{-1} in the molar ratio of 0.6 to 0.8.

Similar phenomena have been observed in the measurement of schoepite solubility for different molar ratios of hypochlorite ion to initial uranyl concentration at fixed pH value (pH 8.3). As shown in Figure 5, total uranium concentration in solution increased with its molar ratio up to 0.06, and then, retained its value in the range of its molar ratio from 0.06 to 0.1. Above this molar ratio, total uranium concentration in solution slowly decreased with the hypochlorite ion concentration.

After solubility measurement, X-ray diffraction pattern for the residual precipitates in both titration vessel was recorded, as shown in Figure 6. Compared with the diffraction pattern of schoepite [8], new dif-

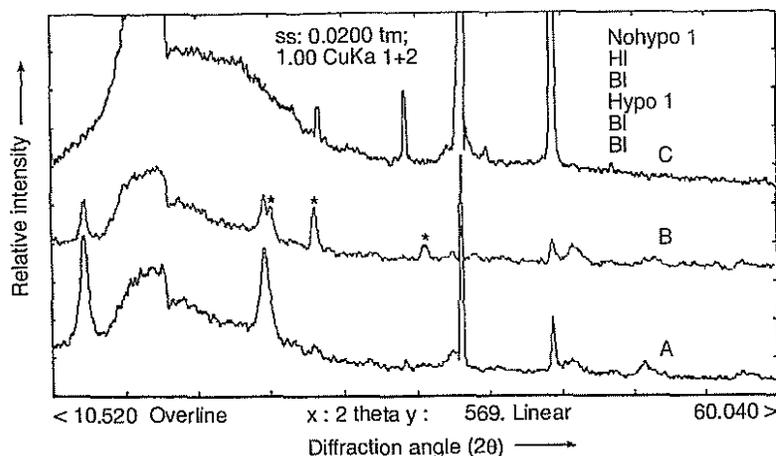


Fig. 6. X-ray diffraction pattern for aged uranyl precipitates (schoepite) without OCl^- (A), with OCl^- (B), and only for MF-Millipore membrane filter (diameter 25 mm) (C).

fraction angles (2θ) at 25.45° , 28.40° and 35.87° were observed in the precipitate with hypochlorite ion. Freshly prepared schoepite with hypochlorite ion and schoepite showed a broad X-ray diffraction patterns, however, they had the same feature and shape as those for aged precipitates.

Discussion

Hypochlorite ion, which is produced by a strong α -radiation in concentrated Cl^- media, has a strong oxidizing ability. In a previous study, it was reported that uranium(IV) was oxidized by hypochlorous acid, a conjugate acid of hypochlorite ion [4]. Hypochlorite ion cannot oxidize uranyl ion (UO_2^{2+}) any further. Solubilities of schoepite in various pH range have been reported by many authors [9], however, there is no information on its solubility in the presence of hypochlorite ion in solution.

The presence of hypochlorite ion in solution enhanced the solubility of schoepite 10 to 100 times in the range of pH 6.0 to pH 9.8, as shown in Figure 1. There would be two possible explanations for the increment in solubility: (1) Hypochlorite ion may interact with schoepite to form a new compound that gives a higher solubility in solution. (2) Hypochlorite ion may substitute one of the hydroxyl group in $(\text{UO}_2)_3(\text{OH})_5^+$ to form a mixed complex, $(\text{UO}_2)_3(\text{OH})_4(\text{OCl})^+$, as in plutonium(VI) [2]. New reaction path for the formation of a mixed complex shifts the equilibrium between schoepite and $(\text{UO}_2)_3(\text{OH})_5^+$, the predominant uranyl species soluble in solution at the neutral pH range. Thus, solubilities are increased due to the formation of a mixed complex. The appearance of a peak shoulder at 311 nm in UV-Vis spectra (Figure 2) gives a good indication for the existence of a new chemical species in solution. Compared with the spectroscopic data for Cl_2 ($\lambda_{\text{max}} = 333 \text{ nm}$, $\epsilon = 65 \text{ M}^{-1} \text{ cm}^{-1}$), HOCl ($\lambda_{\text{max}} = 235 \text{ nm}$, $\epsilon = 100 \text{ M}^{-1} \text{ cm}^{-1}$), and OCl^- ($\lambda_{\text{max}} = 292 \text{ nm}$, $\epsilon = 350 \text{ M}^{-1} \text{ cm}^{-1}$) [10], the peak shoulder at 311 nm does

not correspond to any of those chemical species in aqueous hypochlorite solution. The peak shoulder at 311 nm is a new one, however, there is no characteristic peak to show the interaction of OCl^- with $(\text{UO}_2)_3(\text{OH})_5^+$ quantitatively in UV-Vis spectroscopic analysis.

Best, Clark and Cooney [11] reported the asymmetric stretching vibration frequencies for UO_2^{2+} , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and $(\text{UO}_2)_3(\text{OH})_5^+$ in D_2O solution as 954 cm^{-1} , 938 cm^{-1} , and 916 cm^{-1} , respectively. Vibration frequency (ν_3) for an asymmetric stretching mode of U–O double bond is sensitive to the changes of ligand in equatorial position. As shown in Figure 3, the measured band positions in our study are agreed well with those reported, and FT-IR spectra for uranyl ion in D_2O solution at various pH values clearly revealed the changes of chemical species in solution. At the molar ratio of 0.07, hypochlorite ion does not change the asymmetric stretching vibrational frequency (917.6 nm) of $(\text{UO}_2)_3(\text{OH})_5^+$. In Figure 4, a new absorption band at 933 cm^{-1} appears and the absorption intensity increases with their molar ratios. Changes in the absorption intensity does not correlate with its molar ratios. However, changes in the absorption intensity at 933 cm^{-1} and the appearance of a new absorption band at 933 cm^{-1} with its molar ratio could represent a drastic changes in an asymmetric stretching mode of U–O double bond. It believes that hypochlorite ion may substitute one of the hydroxyl group on the coordination sites of a predominant species, $(\text{UO}_2)_3(\text{OH})_5^+$, in solution.

Because of amorphous nature of schoepite, the freshly prepared precipitates (schoepite) showed a broad band width in X-ray diffraction pattern. However, X-ray diffraction pattern of an aged precipitates clearly showed three new diffraction angles. Though the aged precipitates was still remained in an amorphous state for 4 months, its band width of the X-ray diffraction pattern became narrower with the lapse of time. It implied that the freshly prepared precipitates slowly changed its amorphous state into a crystalline

form. The appearance of new diffraction angles at 25.45°, 28.40° and 35.87° in X-ray diffraction pattern seems to intercalate the hypochlorite ion into an aged precipitates.

Based on these knowledge, it seems that hypochlorite ion could interact with $(\text{UO}_2)_3(\text{OH})_5^+$, a predominant species in solution, to form a mixed complex, and could also introduce into the precipitates. Changes in FT-IR spectra and the appearance of new diffraction angles at 25.45°, 28.40° and 35.87° in X-ray diffraction pattern would support the formation of a mixed complex, as in plutonium(VI)-hypochlorite system, and the introduction of hypochlorite ion into the precipitates, an amorphous schoepite.

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