# THE SOLUBILITY OF URANIUM(IV) HYDROUS OXIDE IN SODIUM HYDROXIDE SOLUTIONS UNDER REDUCING CONDITIONS

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Abstract—The solubility of hydrous UO_2 in sodium hydroxide solutions containing sodium dithionite and/or Zn metal powder as reductants has been measured. The results provide no firm evidence for any amphoteric behavior of U(IV) but do set an upper limit of $K \leq 2 \times 10^{-23}$ for the hypothetical reaction:

$$U^{4+}(aq) + 5H_2O \rightleftharpoons U(OH)_5^- + 5H^+.$$
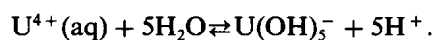
The results provide no evidence for such a reaction.

The hydrolysis behavior of metal cations is a field about which a very large degree of uncertainty exists. In particular, much of the experimental data[1] are highly questionable because of inadequate or improper experimental technique, sparcity of data points, and wide scatter in the data. Often later authors have used such poor or limited experimental data to arrive at conclusions different from and often much beyond those that the original authors were willing to make. An example of this is the calculation of the formation constants of the lanthanide tetrahydroxo complexes[1] from data on the solubility of the $Ln(OH)_3$ in NaOH solutions in which some of the original workers indicated that the experimental results were not adequate for any calculation of species formed[2] and from data of other workers that clearly does not show such a dependence of solubility on NaOH concentration or mean ionic activity[2–4] as to be able to conclude that the $Ln(OH)_4^-$ ions are even being formed.

The solubilities of the actinides at near neutral pH values are of particular importance to the geological disposal of nuclear waste. In particular, the solubility of tetravalent actinides is of importance under the reducing conditions expected in several of the proposed repository environments such as deep basalt or granite. Under these conditions, tetravalent species of U, Np and perhaps Pu become important. There has been a large effort exerted towards prediction of solubilities and modeling of actinide migration behaviour on the basis

of hydrolysis and complex formation equilibria. Much of this equilibrium hydrolysis data has come from limited and poor experimental results or has been estimated by extrapolation from other hydrolysis constants of the same metal ions by what might be considered reasonable but certainly unproven methods.

Specifically, with the tetravalent actinides, almost all of the hydrolysis data for mononuclear species beyond the MOH^{3+} species is based on old and questionable work by Gayer and Leider[5] on the solubility of what they called uranium (IV) hydroxide [actually hydrous U(IV) oxide.[6] Hydrous U(IV)oxide, $UO_{2(am)}$, is *very* easily air-oxidized, and their preparation and handling of the material leaves considerable doubts that they measured U(IV) in solution at all. In addition, their solutions were settled for 3–5 days without filtration. (It is the present authors' observation that centrifuging at 1500 G for up to 1 hr will not totally remove the Tyndall Effect from even fresh suspensions of crystalline UO_2.) They measured U concentrations at six NaOH concentrations, and after discarding two data points that did not fit their conclusions, used only four points to arrive at a first power dependence on OH^- concentration (0.14 to 0.48 M) and calculated an equilibrium constant for formation of $H_3UO_4^-$. Baes and Mesmer[1] assumed this species to be $U(OH)_5^-$ instead of $H_3UO_4^-$ and, making the totally erroneous assumption that Gayer and Leider had used $UO_2(c)$ instead of amorphous hydrous UO_2 (referred to as "$U(OH)_4$" by gayer and Leider,[5] calculated the fifth hydrolysis constant of U(IV). Then, using measured values for the first hydro-

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lysis constant and the perhaps not completely unreasonable but certainly completely unproven assumption that the logarithms of the stepwise hydrolysis constants are linear with respect to the number of hydroxide ions, they calculated values for the formation constants of the $U(OH)_2^{2+}$, $U(OH)_3^+$, and $U(OH)_4$(aq) species. Actually such a concept could be very strongly questioned on several grounds such as for example the fact that there certainly does not appear to be a uniform progression in the hydrolysis of the actinide M^{5+} or M^{6+} ions where *very* strong hydrolysis to the MO_2^+ and MO_2^{2+} ions occurs with little apparent stability for less hydrolyzed species along with a much lower tendency to further hydrolysis. In fact, the tendency of pentavalent and hexavalent actinides to form oxo rather than hydroxo species, and the fact that the tetravalent actinides precipitate as hydrous oxides rather than hydroxides[6] raises a question of whether complexes such as $U(OH)_4$(aq) and $U(OH)_5^-$ exist at all.

Langmuir[7] repeated the same hydrolysis constant estimates for U(IV) made by Baes and Mesmer[1] including the erroneous assumption that there was no free energy change in forming UO_2(c) from the amorphous "$U(OH)_4$" solid used by Gayer and Leider.[5] He calculated free energies of formation for $U(OH)_2^{2+}$, $U(OH)_3^+$, $U(OH)_4$(aq), and $U(OH)_5^-$. It is interesting that Langmuir made the opposite assumption further on in his paper[7] to conclude that $UO_{2(am)}$, which is indeed the same as "$U(OH)_4$," is at least 7.6 kcal/mole less stable than UO_2(c) and may more likely be 12.8 kcal/mole less stable. These erroneous formation constants[7] have been further used,[8] apparently without critical review, to calculate the solubility of amorphous UO_2, as a function of pH. The preposterous conclusion, in terms of well-known U(IV) chemistry, was reached and published[8] that uranium solubility at low (10^{-80}) oxygen fugacity would increase above about pH 4.5 reaching 1 g/L at pH 9.8, and 10 g/L at pH 10.8. Such conclusions appear to be the result of a total loss of contact with the reality of known actinide behaviour and a total preoccupation with the computer manipulation of formation constant data without regard to its validity.

Others[9-12] have repeated similar estimates of U(IV) hydrolysis constants or free energies of formation often giving additionally estimates of entropies, extrapolating to other tetravalent actinides, or giving values as a function of ionic strength. Most of these values are the same or very near those reported by Baes and Mesmer[1] and are based on the limited and questionable results of Gayer and Leider.[5]

Tremaine *et al.*[13] have made a careful attempt to measure the solubility of UO_2(c) under nonoxidizing conditions at high pH. They used deaereated and H_2 saturated LiOH solutions (about 0.003 and 0.04 M) in a flow apparatus with concentration of U by ion exchange followed by neutron activation analysis. Their U solubilities were in the range of about 5×10^{-8} to 1.7×10^{-7} M (seventy-fold lower than the values predicted for these OH^- concentrations for UO_2(am) by Gayer and Leider's[5] results). Their U analyses were apparently near their detection limit due to ^{18}F interference which is directly proportional to the LiOH concentration. Also, they have shown[13] by X-ray photoelectron spectra that during their flow solubility runs below 150°, oxidation of the UO_2 surface beyond the initial 0.3 U(VI)/U(IV) (corresponding to two monolayers of UO_3) occurred up to at least 0.76 U(VI)/U(IV). Their solutions apparently also contained somewhat less than 1% carbonate relative to hydroxide, and they showed based on literature stability constants, that at 10^{-8} M CO_3^{2-} and 10^{-5} atm O_2 the U(VI)/U(IV) ratio in solution should be 10^7. Despite this, they have interpreted their results based on only two OH^- concentrations in terms of the predominant solution species being $U(OH)_5^-$. It is our opinion that they cannot possibly have measured U(IV) solubility as long as U(VI) solid is clearly present, and it is known that U(VI) has a solubility of $\geq 10^{-3}$ M in LiOH solutions in this concentration range[14] (as it also has in $(C_3H_7)_4NOH$[15] and $(C_4H_9)_4NOH$[16] solutions).

The present work reports results of a study of the solubility of amorphous, hydrous UO_2 under anoxic, reducing, alkaline conditions at 25°. Sodium dithionite and metallic zinc were used as reductants in this study.

EXPERIMENTAL

Reagents

Water was in all cases deaerated by boiling following by thorough sparging at 25° with Ar(> 99.99%). A new bottle of reagent grade pellets of NaOH was opened in an Ar atmosphere, and a stock 10.5 M NaOH solution was prepared under Ar. An analysis showed 0.0152 M carbonate. A 7.5% excess of $BaCl_2$ was added, and the closed container was allowed to stand for two weeks under Ar to achieve complete precipitation and settling of the $BaCO_3$. Sodium dithionite was from Sigma Chemical and a 1 M stock solution was prepared under Ar immediately before it was used to make up the first series of solubility solutions.

U(IV) stock solution was prepared by dissolving Hanford reactor grade uranium metal in 12 M HCl (initially with solution cooling but finally with heating to 100°). The hot solution was centrifuged while slow H_2 evolution was still occurring from black residues. The solution (~ 500 g U(IV)/L and ~ 2 M HCl) was then filtered through an 250 nm Millipore Solvinert filter and stored under Ar.

General procedure

All solutions were made up and handled in an Ar atmosphere, and all solution containers were kept closed except for the minimum times necessary for makeup and sampling. Sodium hydroxide solutions (20 cm³) were made by dilution of the stock solution, followed immediately by addition of reductant, and then of the U(IV) solution. The total U present was 0.25 mg/cm³, and by adding it as such a concentrated stock solution, its precipitation and the neutralization of excess acid would be expected to consume only 0.005 M OH⁻, which is 10% of the lowest hydroxide concentration used. All the sealed containers of solution plus hydrous UO₂ were shaken vigorously for 13 or 16 days at room temperature (21 ± 2°). At the end of this equilibration period, the still-sealed containers were centrifuged for 30 min at > 1000 G. Each container was then opened under Ar and the supernatant solution was quickly sampled by syringe. A membrane filter was immediately attached to the syringe, and the solution forced slowly through the filter. The filters in all cases except the ≥ 10 M NaOH solutions were Nuclepore Ultrafilter®, Type F, No. 1F7257, which has a 20,000 molecular weight cutoff for globular proteins (~ 2 nm pore size), and is resistant to OH⁻ solutions. Insufficient flow of ≥ 10 M NaOH could be obtained with this filter, and Millipore Solvinert® filters UGWP with 250 nm pore size were used for these solutions.

Uranium analysis

Uranium analyses were made by laser-induced fluorescence using a Scintrex® model UA-3 uranium analyzer with the known addition technique.[17,18] The samples were pretreated by addition of excess NaOCl (while still basic so that the dithionite would not decompose before it was oxidized) and were then acidified and, except for the samples containing only Zn as reductant, taken to dryness. The residues (principally Na salts) were taken up in dilute HNO₃ and analyzed. The samples containing Zn only as reductant showed a high fluorescence before addition of the buffered complexant used in the method if they had been dried so were taken only to near dryness. The principal

purpose of the drying was to remove excess acid to avoid over-consuming the buffering capacity of the complexant.

Known U standards were, after addition of NaOH, Na₂S₂O₄, etc. taken through the above procedure with accurate recovery. These standards and those used in the known addition technique were prepared from NBS uranium metal standard. Reagent blanks corresponding approximately in composition to some of the samples yielding results below 10^{-8} M were run and gave approximately 80% of the sample values (instrument scale readings were also very low for these) indicating that the true values for samples below 10^{-8} M are in all cases less than those shown.

RESULTS AND DISCUSSION

Tremaine, *et al.*[13] have estimated, based on earlier stability constant estimates[19] using the Gayer and Leider[5] data for U(OH)₅⁻, that K = 3 × 10⁵⁵ for the reaction:

$$U(OH)_5^- + CO_3^{2-} + \tfrac{1}{2}O_2 + 3H^+ \rightleftharpoons UO_2CO_3(aq)$$
$$+ 4H_2O. \quad (1)$$
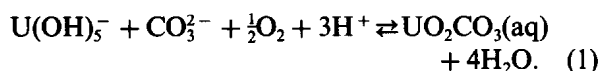
A reasonable estimate for the carbonate concentration at their highest LiOH concentration (0.04 M) would be about 2 × 10⁻⁴ M. This would mean that an O₂ fugacity of less than 10⁻²⁶ would be required to maintain a U(VI)/U(IV) ratio of one in solution. Any lower stability of U(OH)₅⁻ (as reflected by lower U(IV) solubility) would lower the required O₂ fugacity by two orders of magnitude for each order of magnitude lower U(IV) solubility. This alone points to the impossibility of Gayer and Leider's results being correct since they used no reductant for O₂ removal at all. It is also extremely improbable that the H₂ used by Tremaine *et al.*[13] could be a kinetically sufficient reductant to achieve such low fugacities, especially at temperatures below 150°C.

The dithionite ion is known to be a strong reductant with $E_B^\circ = 1.12V^{19}$ for the reaction:

$$S_2O_4^{2-} + 4OH^- \rightleftharpoons 2SO_3^{2-} + 2H_2O + 2e^-. \quad (2)$$
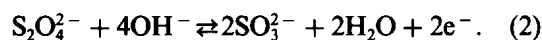
It is known that alkaline dithionite solution reacts with oxygen rather rapidly,[20] and it was found that when 1–10 g U(VI)/L solutions in (C₃H₇)₄NOH were warmed with dithionite (or the related Rongolite), reduction and precipitation of U(IV) hydrous oxide occurred. Based on the above potential, it can be shown that the thermodynamic equilibrium oxygen fugacity in NaOH solutions above 0.01 M and containing 50% oxidized dithionite would be below 10⁻⁹⁰. Zinc metal is slightly

more reducing with $E_B^{\circ} = 1.216V^{19}$ for the reaction:

$$Zn + 4OH^- \rightleftharpoons ZnO_2^{2-} + 2H_2O + 2e^- \qquad (3)$$
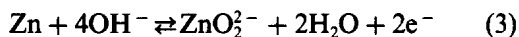
and the ZnO_2^{2-} ion is sufficiently stable[19], with $K = 1 \times 10^{-29}$ for:

$$Zn(OH)_2 \rightleftharpoons ZnO_2^{2-} + 2H^+ \qquad (4)$$
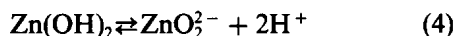
to maintain small amounts of Zn in solution and not form $Zn(OH)_2$ at the OH^- concentrations of interest here. Zn metal will also thermodynamically keep O_2 fugacity below 10^{-90} above 0.01 M NaOH, but because it is a solid may not be kinetically adequate. Using the reductants discussed above, solubility measurements were made in three series of solutions. The principal series was in dithionite solution while fewer measurements were made with zinc metal or zinc metal plus dithionite.

Carbonate was removed from the stock 10.5 M NaOH with $BaCl_2$ at an 0.0012 M excess. If activity coefficients are neglected (they should be greater than one in 10.5 M NaOH), a CO_3^{2-} concentration in this stock solution of 5×10^{-6} M is obtained based on the published[21] solubility product for $BaCO_3$. The values for the individual solutions will vary with the dilution factor from this stock solution.

Table 1 gives measured total uranium concentrations in the dithionite containing solutions of NaOH in contact with hydrous UO_2. The solu-

bilities are shown in Figure 1 along with those of Gayer and Leider[5] as a function of mean ionic activity of NaOH using activity coefficient data of Hamer and Wu.[22] The solid line corresponds to the formation constant reported by Gayer and Leider. Over the concentration range where the Gayer and Leider measurements were made, the values measured here are all 10^3 to 10^4-fold lower than those of Gayer and Leider and all values are, as discussed in the experimental section, almost at the reagent blank level so they must be considered at the detection limit and are upper limits on the true solubility. Since they are upper limits, no significance can be placed on a possible slope in this region. At higher NaOH concentrations, there is greater than an order of magnitude scatter in the total U concentration data so again a slope cannot be determined.

Table 2 gives measured total uranium concentrations in NaOH solutions containing metallic zinc powder and hydrous UO_2. These results are also shown in Fig. 1 as a function of mean ionic activity of NaOH. The measured solubilities with Zn as a reductant are higher at low NaOH concentrations and lower at high NaOH concentrations than those with dithionite as the reductant. It was observed that at 10 M NaOH, most of the sodium dithionite actually precipitated from solution. Also, because of the increasing stability of the

Table 1. Measured U(IV) hydrous oxide solubility in NaOH-0.05 M $Na_2S_2O_4$ solutions

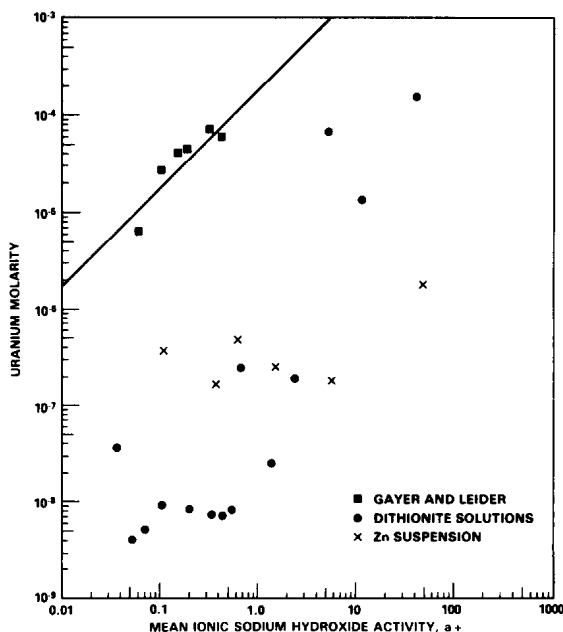| NaOH Molarity	U Molarity
0.045	3.6×10^{-8}
0.070	4×10^{-9}
0.095	5×10^{-9}
0.145	9×10^{-9}
0.295	8×10^{-9}
0.50	7×10^{-9}
0.65	7×10^{-9}
0.80	8×10^{-9}
1.00	2.4×10^{-7}
2.00	2.5×10^{-8}
3.00	1.9×10^{-7}
5.0	6.7×10^{-5}
7.0	1.3×10^{-5}
10.0	1.5×10^{-4}

Fig. 1. Measured apparent solubilities of hydrous U(IV) oxide in sodium hydroxide solutions. Results of Gayer and Leider are from Ref. 5. Dithionate solutions were initially 0.05 M $Na_2S_2O_4$ and Zn suspensions were initially 1.6 mg Zn/cm³.

Table 2. Measured U(IV) hydrous oxide solubility in
initially 1.6 mg Zn/cm^3 suspensions in NaOH

NaOH Molarity	U Molarity
0.153	5.0×10^{-7}
0.55	1.64×10^{-7}
1.05	4.6×10^{-7}
2.10	2.48×10^{-7}
5.2	1.81×10^{-7}
10.5	1.81×10^{-6}

Table 3. Measured U(IV) hydrous oxide solubility in
NaOH-0.05 M Na$_2$S$_2$O$_4$ solutions containing initially
1.6 mg Zn/cm^3

NaOH Molarity	U Molarity
0.145	5.46×10^{-8}
0.50	7.98×10^{-7}
1.00	8.82×10^{-7}
2.00	2.28×10^{-6}
5.0	8.4×10^{-6}

ZnO$_2^{2-}$ ion relative to Zn(OH)$_2$ or ZnO at high hydroxide concentrations, it might be expected that any coating initially present or forming on the Zn surface might be more readily removed at higher alkalinity making Zn kinetically more effective at the higher hydroxide concentrations. At lower ($< 1 M$) NaOH concentration, the higher apparent solubilities with Zn reductant may be due to poorer kinetics of oxygen scavenging or might possibly be due to uranium complexing by ZnO$_2^{2-}$ ion. In any case, all values are much below those predicted by the results of Gayer and Leider.[5]

Table 3 gives measured total uranium concentrations in NaOH solutions containing both dithionite and Zn metal powder. Despite the fact that the values in Table 3 are all at least two orders of magnitude lower than predicted by the results of Gayer and Leider, they are higher in all cases but one than the values for dithionite alone, and in all but one other case than values for Zn alone. The reason for this is not clear; the dithionite stock solution was 2 weeks old when used to make up the solutions used for the data of Table 3, whereas it was less than 1 hr old when used for make up of solutions in Table 1. Also, it was visually observed that the finer Zn particles dissolved during equilibration in the Zn-only suspensions (Table 2), whereas they did not appear to react at all in the dithionite–zinc mixtures (Table 3) indicating preferential consumption of dithionite in the latter.

Overall, it is much more probable that erroneously high results rather than erroneously low results will be obtained in the solubility experiments described here. In all cases here, solubility was approached from the over-saturated side. As noted earlier, very low oxygen fugacities are expected to be required to maintain U(IV) in these alkaline solutions, and since U(VI) is much more soluble than U(IV), high values would be expected if incomplete oxygen scavenging occurred. In this regard, the higher observed solubilities in dithionate solutions above 1 M OH$^-$ may be due to

poorer oxygen scavenging, U(VI) reduction, or precipitation kinetics in these increasingly viscous solutions. It should also be noted that CO$_3^{2-}$ concentration is proportional to OH$^-$ concentration in these solutions, and carbonate complexing is expected to increase the stability of U(VI). Any-cross-contamination resulting from working in the same inert atmosphere chamber for solution makeup with very concentrated U solutions and for solution sampling and filtering would also yield an erroneously high result.

The only way that low results could be expected would be if the analytical method did not respond to the total uranium present. All of the results given are based on more than one analysis (many on several with good agreement). In all cases, analysis was based on the technique of known addition whereby appropriate standards were added after the sample reading was obtained and a new reading measured. In addition, in many cases standards were added either to aliquots of samples which had not been pretreated or to NaOH-Na$_2$S$_2$O$_4$ solution, and these were taken through the entire procedure with excellent standard recovery. In order to show that soluble U was not removed by ion exchange or other reaction with the filter material, the solution shown in Table 1 as 0.295 M NaOH was, after initial sampling for filtration, resealed, and was centrifuged at > 1000 G for 24 hr and a sample taken without filtering analyzed $1.3 \times 10^{-8} M$ U vs $8 \times 10^{-9} M$ (or background level) with filtering. Thus, it must be concluded that the solubility values of $< 10^{-8} M$ in the range 0.1 to 1 m NaOH in dithionite solution are real, and that the results of Gayer and Leider are at least four orders of magntiude too high.

CONCLUSIONS

Based on the above discussion, only the lowest measured U concentrations at a given NaOH concentration should be considered as an upper

limit for U(IV) solubility. The results do not provide solid evidence for any amphoteric behavior of U(IV) despite the measured solubility values being higher above 1 M NaOH. It is by no means certain that the measured U in any of these solutions was present as U(IV). The data presented indicate that the solubility of U(IV) hydrous oxide is at least four orders of magnitude lower than predicted by the results of Gayer and Leider,[5] and that their equilibrium constant for the formation of U(OH)$_5^-$, if such indeed is a dominant species at all in this OH$^-$ concentration range, is at least four orders of magnitude too large. In other words, $K \leq 1.7 \times 10^{-8}$ for the reaction:

$$UO_2(am) + 2H_2O + OH^- \rightleftharpoons U(OH)_5^-. \quad (5)$$

Using the conservative value of Langmuir[7] for the free energy of formation of amorphous UO_2 and assuming that this applies to the 2-week old precipitated hydrous UO_2 used here, gives a limit for $\Delta G_f \geq -379.4$ kcal/mole for U(OH)$_5^-$. Using $\Delta G_f = -126.9$ kcal/mole for $U_{(aq)}^{4+}$[7,23], yields a value of $K \leq 2 \times 10^{-23}$ for the reaction:

$$U^{4+}(aq) + 5H_2O \rightleftharpoons U(OH)_5^- + 5H^+ \quad (6)$$

vs a value of 10^{-16} reported by Baes and Mesmer.[1] Such a value yields a solubility of crystalline UO_2 as U(IV) of $< 10^{-14} M$ at 1 M NaOH.

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