

# Solubility of U(VI) in chloride solutions. I. The stable oxides/hydroxides in NaCl systems, solubility products, hydrolysis constants and SIT coefficients

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## A B S T R A C T

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The solubility of uranium(VI) is studied at  $T = (22 \pm 2)^\circ\text{C}$  in carbonate free  $0.03\text{--}5.61\text{ mol}\cdot\text{kg}_w^{-1}$  NaCl solutions at  $\text{pH}_m = 4\text{--}14.5$  ( $\text{pH}_m = \log[\text{H}^+]$ ). The solid phases metaschoepite  $\text{UO}_3\cdot 2\text{H}_2\text{O}(\text{cr})$  and sodium uranate  $\text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O}(\text{cr})$  (or  $\text{NaUO}_2\text{O}(\text{OH})(\text{cr})$ ) are characterized by XRD, SEM EDS, thermogravimetry and quantitative chemical analysis.  $\text{UO}_3\cdot 2\text{H}_2\text{O}(\text{cr})$  controls the solubility of U(VI) in acidic to near neutral pH conditions regardless of NaCl concentration.  $\text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O}(\text{cr})$  forms in alkaline systems and is stable at  $\text{pH}_m \geq 7$  over the complete range of NaCl concentrations investigated.

The solubility of  $\text{UO}_3\cdot 2\text{H}_2\text{O}(\text{cr})$  at  $\text{pH}_m < 7$  in NaCl solutions is very well described with the hydrolysis constants recommended by the NEA TDB, a set of SIT coefficients evaluated in the present study and a solubility product of  $\log^* K_{s,0}^\circ\{\text{UO}_3\cdot 2\text{H}_2\text{O}(\text{cr})\} = (5.35 \pm 0.13)$ . Titration experiments and UV-vis absorption spectra of saturated solutions at  $\text{pH}_m = 4\text{--}5$  in dilute to concentrated NaCl solutions confirm the speciation calculated in the present study and show the predominance of the trinuclear hydroxide complex  $(\text{UO}_2)_3(\text{OH})_4^{2+}$  at high chloride concentrations. Solubility data obtained at  $7 \leq \text{pH}_m \leq 14.5$  with  $\text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O}(\text{cr})$  and in solutions equilibrated simultaneously with  $\text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O}(\text{cr})$  and  $\text{UO}_3\cdot 2\text{H}_2\text{O}(\text{cr})$  yield a solubility product of  $\log^* K_{s,0}^\circ\{0.5\text{ Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O}(\text{cr})\} = (12.2 \pm 0.2)$  and the formation constants of the anionic hydrolysis species  $\text{UO}_2(\text{OH})_3^-$  ( $\log^* \beta_{(1,3)}^\circ = (20.7 \pm 0.4)$ ) and  $\text{UO}_2(\text{OH})_4^{2-}$  ( $\log^* \beta_{(1,4)}^\circ = (31.9 \pm 0.2)$ ). SIT coefficients for these species are derived based on the solubility data obtained in dilute to concentrated NaCl systems.

The chemical, thermodynamic and SIT activity models provided in this work for the system  $\text{U}^{\text{VI}}\text{--Na}^+\text{--H}^+\text{--Cl}^-\text{--OH}^-\text{--H}_2\text{O}(\text{l})$  represent an accurate and robust tool for the calculation of U(VI) solubility and aqueous speciation in a variety of geochemical conditions relevant in the context of nuclear waste disposal.

## 1. Introduction

Performance assessment calculations related to the safety of nuclear waste disposal in underground repositories may require the geochemical modelling of the solubility and aqueous speciation of U(VI) in dilute to concentrated NaCl brines with chloride concentrations up to  $6\text{ mol}\cdot\text{kg}_w^{-1}$ . The chemical thermodynamics of solid and aqueous uranium compounds and complexes have been investigated since many decades by a large number of authors. The present knowledge is summarized in the reviews of the OECD/

Nuclear Energy Agency Thermochemical Databases (NEA TDB) [1,2]. However, despite of the amount of work done in this field, there is no systematic data set available which allows the reliable prediction of U(VI) solubility and aqueous speciation covering entire pH range in dilute to concentrated brine solutions. The solubility behavior of limiting oxide/hydroxide phases formed in concentrated NaCl solutions are not well ascertained and there are no ion interaction coefficients to calculate reliable activity coefficients and formation constants of hydroxide complexes in saline solutions above  $3\text{ mol}\cdot\text{kg}_w^{-1}$ .

Numerous solubility studies with more or less crystalline metaschoepite  $\text{UO}_3\cdot 2\text{H}_2\text{O}(\text{cr})$  or  $\text{UO}_2(\text{OH})_2(\text{s, hydr})$  have been reported during the last decades [3–12]. Although the calculation

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of the solubility products is partly based on different hydrolysis schemes and constants, the published values are, after conversion to  $I=0$  (c.f. [2]), in reasonable agreement and yield an average value of  $\log K_{s,0}^{\circ} = (5.2 \pm 0.4) (2\sigma)$  ( $\log K_{s,0}^{\circ} = (22.8 \pm 0.4)$ ). Ternary M U(VI) OH(s) solid phases are known to form under near neutral to alkaline pH conditions in the presence of alkaline and alkaline earth cations. Several experimental studies have investigated the formation and solubility of Na containing U(VI) solid phases at room temperature [9,12–14]. Yamamura et al. [13] investigated the solubility of  $\text{Na}_2\text{U}_2\text{O}_7 \cdot x\text{H}_2\text{O}(\text{cr})$  (with  $x = 3–5$ ) in the  $\text{NaOH}–\text{CO}_3–\text{ClO}_4–\text{H}_2\text{O}(\text{l})$  system, and reported a solubility product of  $\log K_{s,0}^{\circ} = (29.45 \pm 1.04)$ . Comparable results were reported by Meinrath et al. in carbonate free NaCl and  $\text{NaClO}_4$  solutions [14]. Diaz Arocas and Grambow (1998) investigated the precipitation of U(VI) solid phases in dilute to concentrated NaCl solutions at pH 4–6 [15]. Based on their solubility data in 3 mol  $\text{kg}_w^{-1}$  NaCl solutions, the authors determined a  $\log K_{s,0}^{\circ} = (7.13 \pm 0.15)$  for the equilibrium reaction  $\text{Na}_{0.33}\text{UO}_{3.165} \cdot 2\text{H}_2\text{O}(\text{cr}) + 2.33 \text{H}^+ \rightleftharpoons 0.33 \text{Na}^+ + \text{UO}_2^{2+} + 3.165 \text{H}_2\text{O}(\text{l})$  [15]. Under these experimental conditions, however, this solid phase is expectedly metastable with respect to  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$ . Giammar et al. (2002, 2004) [9,16] studied solid phase transformations of  $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$  (soddyite) and  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  in  $\text{NaNO}_3$  and NaF systems at  $\text{pH} \approx 6$ . The formation of a clarkite like solid phase ( $\text{Na}(\text{UO}_2)\text{O}(\text{OH})(\text{s})$ ) was reported in both cases based on an extended solid phase characterization. Gorman Lewis et al. (2008) [12] performed undersaturation and oversaturation solubility experiments starting with  $\text{Na}(\text{UO}_2)\text{O}(\text{OH})(\text{s})$  in  $\text{NaNO}_3$  solutions with  $\text{pH} = 4.2–6.4$ . Partial or complete solid phase transformation to  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  was observed in all experimental batches depending upon pH and  $[\text{NaNO}_3]$ . The solubility product of  $\text{Na}(\text{UO}_2)\text{O}(\text{OH})(\text{s})$  was reported as  $\log K_{s,0}^{\circ} = 9.4 (0.9/+0.6)$ .

A large number of U(VI) oxide and hydroxide solid phases are discussed in the NEA TDB reviews [1,2] in terms of crystallinity, crystal structure and number of hydration waters. The thermodynamic selection for these solid phases is based on thermochemical studies and does not consider solubility data. Hence, the standard molar Gibbs energies selected in the NEA TDB [1,2] for well crystallized metaschoepite ( $\Delta_f G_{\text{m}}^{\circ}(\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})) = (1636.506 \pm 1.7) \text{ kJ mol}^{-1}$ ) and anhydrous sodium diuranate ( $\Delta_f G_{\text{m}}^{\circ}(\text{Na}_2\text{U}_2\text{O}_7(\text{cr})) = (3011.45 \pm 4.02) \text{ kJ mol}^{-1}$ ) are based on calorimetric data. Combined with auxiliary data for  $\text{Na}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ , and  $\text{UO}_2^{2+}$  they correspond to solubility products of  $\log K_{s,0}^{\circ} = (23.2 \pm 0.4)$  and  $(30.7 \pm 0.5)$  ( $\log K_{s,0}^{\circ} = (4.8 \pm 0.4)$  and  $(11.3 \pm 0.5)$ ), respectively. These calculated solubility products are noticeably lower than those determined from solubility studies.

The equilibrium constants selected in the NEA TDB [1,2] for cationic U(VI) hydroxide complexes  $\text{UO}_2\text{OH}^+$ ,  $(\text{UO}_2)_2(\text{OH})_3^+$ ,  $(\text{UO}_2)_2(\text{OH})_2^{2+}$ ,  $(\text{UO}_2)_3(\text{OH})_4^+$ ,  $(\text{UO}_2)_3(\text{OH})_5^+$  and  $(\text{UO}_2)_4(\text{OH})_7^+$  primarily rely on potentiometric studies in  $\text{NaClO}_4$  solutions [4,17–21]. Brown [21] simultaneously evaluated thermodynamic data obtained in potentiometric studies in perchlorate, chloride and nitrate media, and obtained very similar results as those data selected in Ref. [2]. The spectroscopic studies of Meinrath et al. [18–20] suggest that  $\text{UO}_2^{2+}$ ,  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  and  $(\text{UO}_2)_3(\text{OH})_5^+$  are the main U(VI) species forming in acidic 0.1 mol  $\text{L}^{-1}$   $\text{NaClO}_4$  solutions, although the equilibrium constants determined spectroscopically are considerably lower than those obtained in potentiometric studies. For the neutral and anionic complexes  $\text{UO}_2(\text{OH})_2(\text{aq})$ ,  $\text{UO}_2(\text{OH})_3$ ,  $\text{UO}_2(\text{OH})_4^{2-}$  and  $(\text{UO}_2)_3(\text{OH})_7^-$ , only rough estimates could be evaluated by Grenthe et al. [1]. In the last update of the NEA TDB [2], the solvent extraction study of Choppin and Mathur [17] and U(VI) solubility studies in alkaline phosphate and carbonate solutions [4,13] were used to select better approximations for the equilibrium constants of these species.

A number of potentiometric, spectroscopic and calorimetric studies have been published since the last update volume of the NEA TDB [22–27]. De Stefano et al. (2002) conducted a potentiometric study on the hydrolysis of U(VI) in dilute to concentrated NaCl and  $\text{NaNO}_3$  media [22]. The authors discussed the impact of the medium on the hydrolysis reactions, and reported the formation of the species  $\text{UO}_2\text{OH}^+$ ,  $(\text{UO}_2)_2(\text{OH})_2^{2+}$ ,  $(\text{UO}_2)_3(\text{OH})_4^{2+}$  and  $(\text{UO}_2)_3(\text{OH})_5^+$  with equilibrium constants in good agreement with the thermodynamic selection in Ref. [2]. On the contrary, the equilibrium constant reported for the (37) complex is about three orders of magnitude greater than the current NEA TDB selection. The potentiometric and calorimetric studies by Crea et al. (2004, 2005) [23,26] and Zanonato et al. (2004, 2012, 2014) [25,27,28] reported thermodynamic data consistent with De Stefano and co-workers [22], including also the large disagreement with the NEA TDB for the (37) complex. Zanonato et al. (2014) proposed also the formation of other trimers not selected in the NEA TDB, namely  $(\text{UO}_2)_3(\text{OH})_6(\text{aq})$  and  $(\text{UO}_2)_3(\text{OH})_8^-$ . The authors performed their experiments in 0.1 mol  $\text{L}^{-1}$  tetramethyl ammonium nitrate (TMA  $\text{NO}_3$ ) to avoid the precipitation of M(I) U(VI) OH(s) solid phases (with  $M = \text{Na}, \text{K}, \text{etc.}$ ) under the conditions of their experiments ( $7 \cdot 10^{-4} \text{ mol L}^{-1} \leq [\text{U(VI)}]_0 \leq 2 \cdot 10^{-3} \text{ mol L}^{-1}$ ), and thus the presence of polyatomic species not forming in solubility studies imposing lower  $[\text{U(VI)}]$  is reasonable.

In spite of the numerous experimental studies focussing on U(VI) solution chemistry in a variety of boundary conditions, there is no systematic dataset available allowing the reliable prediction of the solubility and aqueous speciation covering entire pH range in dilute to concentrated salt systems. In this context, the present study aims at comprehensive investigation of U(VI) solubility and hydrolysis in dilute to concentrated NaCl solutions. Solubility experiments are complemented with spectroscopic data of the aqueous phase, and the characterization and identification of the stable, solubility limiting U(VI) oxides/hydroxides in NaCl solutions. The hydrolysis scheme of U(VI) dominating in these salt systems is comprehensively evaluated by using new data derived in the present study and findings previously reported in literature. The final aim consists in developing complete chemical, thermodynamic and SIT activity models for the system  $\text{U}^{\text{VI}}–\text{Na}^+–\text{H}^+–\text{Cl}^-–\text{OH}^-–\text{H}_2\text{O}(\text{l})$ , thus providing scientifically sound solubility limits for source term estimations and realistic U(VI) speciation schemes under boundary conditions relevant for nuclear waste disposal.

## 2. Experimental

### 2.1. Chemicals

NaCl (p.a.) and HCl Titrisol® were purchased from Merck. A standard solution of carbonate free NaOH (Baker) was used to adjust the pH of the samples. All solutions were prepared with purified water (Milli Q academic, Millipore) and purged with Ar for 2 h before use to avoid  $\text{CO}_2$  in solution. All sample preparation and handling was performed in an Ar glove box at  $T = (22 \pm 2) ^\circ\text{C}$  and  $P = (1.01 \pm 0.01) \text{ bar}$ .

A table of all chemicals and compounds used in the present study is given in Table A1 as Supporting Information.

### 2.2. pH measurements

The hydrogen ion concentration ( $\text{pH}_m = -\log [\text{H}^+]$ , in molal units) was measured using combination pH electrodes (type ROSS, Orion) calibrated against standard pH buffers (pH 2–12, Merck). The values of  $\text{pH}_m = \text{pH}_{\text{exp}} + A_m$  were calculated from the operational “measured”  $\text{pH}_{\text{exp}}$  using empirical correction factors ( $A_m$ ),

which entail both the liquid junction potential of the electrode and the activity coefficient of  $H^+$ .  $A_m$  values determined as a function of NaCl concentration are available in the literature [29]. The uncertainty in the  $pH_m$  measurements was generally  $\pm 0.05$ , except within  $6 \leq pH_m \leq 8$  where it increased to  $\pm 0.1$ . In NaCl NaOH solutions with  $[OH^-] > 0.03 \text{ mol L}^{-1}$ , the  $H^+$  concentration was calculated from the given  $[OH^-]$  and the conditional ion product of water.

### 2.3. Solid phase preparation and characterization

Metaschoepite,  $UO_3 \cdot 2H_2O(cr)$ , was prepared under protective atmosphere by very slow titration ( $\approx 25 \mu\text{L}/5 \text{ min}$ ) of 200 mL of a  $0.01 \text{ mol L}^{-1}$  solution of uranyl nitrate ( $UO_2(NO_3)_2 \cdot 6H_2O$ , Merck) with  $0.05 \text{ mol L}^{-1}$  carbonate free NaOH. An automatic titroprocessor 686 (Metrohm) was used to add minute amounts of the NaOH solution into the strongly agitated uranium containing solution up to the quantitative precipitation of metaschoepite in the pH range 4–5. The resulting solid phase was aged for one week, washed several times with water and dried under Ar atmosphere at room temperature.

Sodium uranate,  $Na_2U_2O_7 \cdot xH_2O(cr)$ , was prepared by solid phase transformation of metaschoepite under alkaline pH conditions. A uranyl nitrate solution was first quantitatively precipitated to pale yellow metaschoepite in  $1.0 \text{ mol L}^{-1}$  NaCl at  $pH = 4–5$  following the approach described above. The metaschoepite was then quickly titrated to  $pH = 11$ . The solid phase transformation was completed within one week, resulting in an intense yellow orange compound. Sodium diuranate was aged for several months at  $pH = 11$  in frequently stirred  $1.0 \text{ mol L}^{-1}$  NaCl.

The synthesized solid phases were characterized by X ray diffraction (XRD), scanning electron microscopy energy dispersive spectrometry (SEM EDS), quantitative chemical analysis and thermogravimetric analysis (TG DTA) before and after solubility experiments. XRD measurements were performed on a Bruker AXS D8 Advance X ray powder diffractometer at  $5 \leq 2\theta \leq 60^\circ$  with incremental steps of  $0.01^\circ–0.04^\circ$  and a measurement time of 4–30 s per step. SEM EDS was used for the microscopic determination of the crystallite size of the oxides or hydroxides, and for monitoring changes in the morphology and the chemical composition in the course of solubility experiments. SEM pictures were taken with a CamScan CS 44 FE (Cambridge Instruments) equipment. Thermogravimetry (TG) and differential thermal analysis (DTA) were simultaneously carried out under Ar atmosphere using a Netzsch (model STA 449 C Jupiter) equipment with a DSC (difference scanning calorimetry) measuring head. Measurements were performed with 20–50 mg of the solid phase, which were heated up to  $800^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}$  per minute. Quantitative chemical analysis was performed by ICP MS (inductively coupled plasma mass spectrometry) with a Perkin Elmer ELAN 6100 equipment and ICP OES (inductively coupled plasma optical emission spectroscopy) with a Perkin Elmer Optima 2000™ equipment to determine the content of U and Na in the solid, respectively.

### 2.4. Solubility measurements

The solubility of well defined  $UO_3 \cdot 2H_2O(cr)$  and  $Na_2U_2O_7 \cdot xH_2O(cr)$  solid phases was studied from undersaturation conditions at  $T = (22 \pm 2)^\circ\text{C}$ .  $UO_3 \cdot 2H_2O(cr)$  was equilibrated in independent batch samples with 0.03, 0.51, 2.64 and  $5.61 \text{ mol kg}_w^{-1}$  NaCl at  $pH_m \leq 7$ . A second series of batch samples with  $Na_2U_2O_7 \cdot xH_2O(cr)$  was prepared in 0.51, 2.64 and  $5.61 \text{ mol kg}_w^{-1}$  NaCl NaOH solutions at  $8 \leq pH_m \leq 14.5$ . A third series of samples in 0.51, 2.64 and  $5.61 \text{ mol kg}_w^{-1}$  NaCl systems was prepared in the presence of both  $UO_3 \cdot 2H_2O(cr)$  and  $Na_2U_2O_7 \cdot xH_2O(cr)$ , aiming at the characterization of the equilibrium between both solid phases. Small aliquots of 0.01

and  $0.1 \text{ mol L}^{-1}$  HCl NaCl/NaCl NaOH solutions of appropriate ionic strength were used to adjust the  $pH_m$  of individual batch samples to the targeted values.  $pH_m$  and  $[U]$  were measured at regular time intervals from 5 to 200 days. Thermodynamic equilibrium was assumed after repeated measurements with constant  $[U]$  and  $pH_m$  which was normally attained within 20–30 days. The concentration of U 238 was measured by ICP MS after phase separation by ultrafiltration ( $10 \text{ kD} \approx 2 \text{ nm}$ , Pall Life Science). Aliquots of the original samples were diluted 1:10 to 1:1000 times (depending upon salt concentration) with 2%  $HNO_3$  before ICP MS measurements. Blank measurements resulted in 0.001–0.002 ppb of U 238, which corresponded to detection limits of  $\approx 10^{-8}$  to  $\approx 10^{-10} \text{ mol L}^{-1}$  in the original solution (depending upon dilution factor). The accuracy of ICP MS measurements was  $\pm 2–5\%$ . The analytical uncertainty of the ICP MS measurements is always substantially lower than the scattering of the solubility data in the lower concentration range. Such scattering is generally attributed to problems in the phase separation, including sorption phenomena or incomplete separation of colloids [30–32]. Note that all uncertainties reported throughout the text refer to  $2\sigma$ .

The aqueous speciation of uranium was investigated by potentiometric titrations with the aim of determining the OH:U ratio in the uranium species prevailing in solution. A fraction of the supernatant solution of selected solubility samples in 0.51, 2.64 and  $5.61 \text{ mol kg}_w^{-1}$  NaCl systems was treated by ultrafiltration to remove colloids and eventually suspended solid phase particles. Samples were titrated to  $pH_m \approx 2$  with HCl NaCl solutions of appropriate ionic strength (0.51, 2.64 and  $5.61 \text{ mol kg}_w^{-1}$ ) and  $[H^+] = 0.5 \text{ mol kg}_w^{-1}$ . Binary  $UO_2Cl_n^{2-n}$  species are predominant at  $pH_m \approx 2$ .  $H^+$  concentration was measured with a glass electrode (type ROSS, Orion) as a function of added HCl. Supernatant solutions were also characterized by UV vis before and after titration experiments. Absorption data were collected within  $350 \leq \lambda [nm] \leq 500$  using a high resolution UV vis/NIR spectrometer Cary 5 (Varian, USA).

## 3. Results and discussion

### 3.1. Solid phase characterization

XRD diffraction patterns of the U(VI) solid phase prepared under acidic conditions perfectly match those of  $UO_3 \cdot 2H_2O(cr)$  (JCPDS file Nr. 43 0364) (Fig. 1a). SEM images (Fig. 2) show the formation of orthorhombic, lamellar crystals with an edge length of 30 nm to 2–5  $\mu\text{m}$ , grown together into larger aggregates. DTA analysis confirms the presence of two water molecules per uranium atom. XRD patterns of solid phases collected from selected solubility samples in acidic NaCl solutions indicate that the original  $UO_3 \cdot 2H_2O(cr)$  solid phase remained unaltered in the course of the experiments (Fig. 1a).

U(VI) solid phases equilibrated in alkaline NaCl solutions show XRD patterns with close similarities to clarkeite ( $NaUO_2O(OH)(cr)$ , JCPDS file Nr. 87 1714) and  $NaUO_2O(OH) \cdot H_2O(cr)$  (JCPDS file Nr. 50 1586) (Fig. 1b). It also shows XRD reflections similar to other sodium uranate phases, such as  $Na_6U_7O_{24}(cr)$  (JCPDS File Nr. 05 0446). Analogous XRD patterns were reported in previous studies investigating the solubility of U(VI) in neutral to alkaline Na containing systems [9,13,14]. Fig. 1b shows also that solid phases collected after terminating the solubility experiments in alkaline 0.51, 2.64 and  $5.61 \text{ mol kg}_w^{-1}$  NaCl systems retain the same XRD patterns of the original material, thus indicating that no transformation of the solid phase took place during the solubility experiments. XRD characterization of  $UO_3 \cdot 2H_2O(cr)$  equilibrated in  $0.03 \text{ mol kg}_w^{-1}$  NaCl at  $pH_m = 11$  showed the incomplete transformation into the sodium uranate phase stable in more concentrated

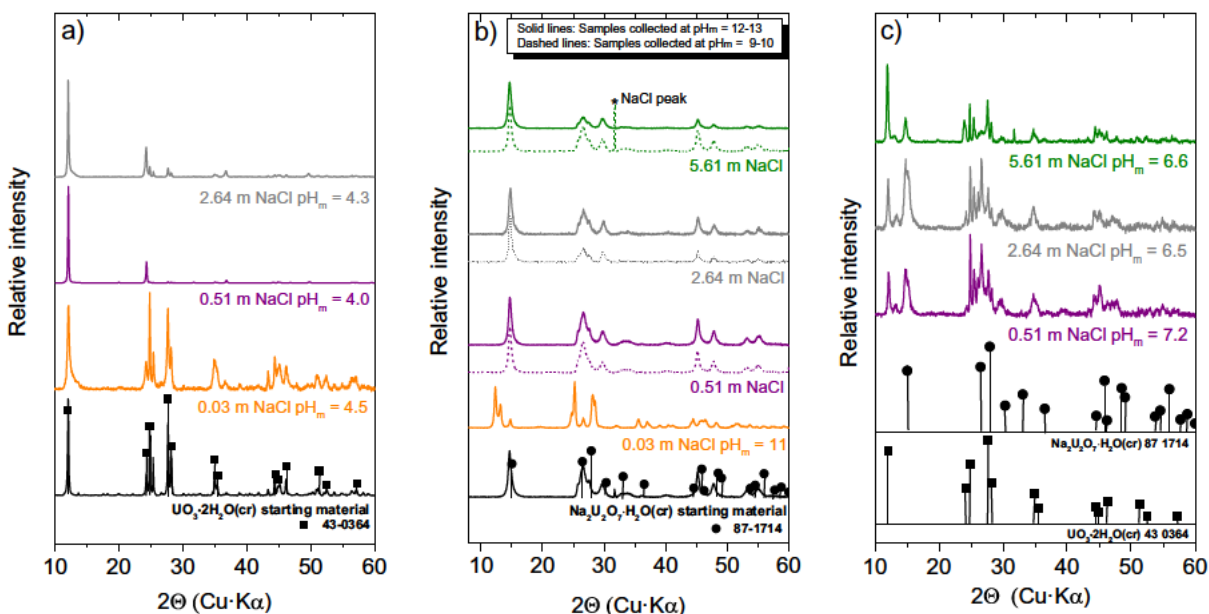


Fig. 1. XRD patterns of selected solid phases from solubility experiments in dilute to concentrated NaCl solutions: (a) acidic pH region,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  as starting material; (b) alkaline pH region,  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$  as starting material; (c) solubility samples equilibrated with both  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  and  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$ . Squares and circles mark peak positions and relative intensities reported for  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  (JCPDS file Nr. 43-0364) and  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$  (JCPDS file Nr. 87-1714). XRD patterns at the bottom of figures (a) and (b) correspond to the starting  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  and  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$  solids used in the solubility experiments in acidic and alkaline pH conditions, respectively.

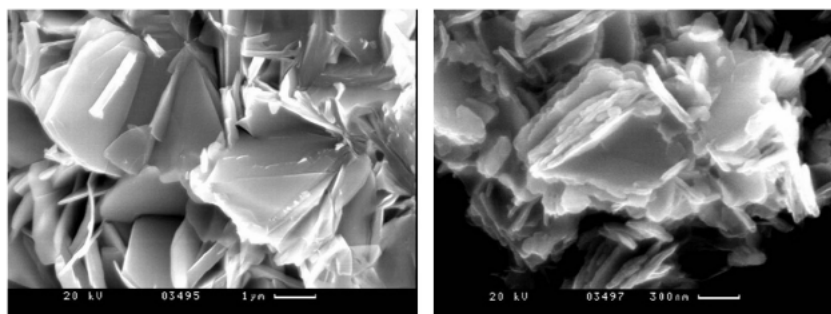


Fig. 2. Left: SEM pictures of the precipitated and aged  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  solid phase used as starting material. Right: SEM picture of initial  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$  transformation product investigated in the solubility experiments.

NaCl systems. The SEM image of Na uranate provided in Fig. 2 shows coalesced, plate shaped crystals of about 30 nm thickness and diameters of up to 2 μm. DTA analysis of the dried solid phase indicates a content of 0.5 water molecules per uranium atom, whereas quantitative chemical analysis resulted in a Na:U ratio of  $0.9 \pm 0.1$ . Based on these results, the chemical formula of the solid controlling the solubility in alkaline dilute to concentrated NaCl systems can be defined as  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$  or  $\text{NaUO}_2\text{O}(\text{OH})(\text{cr})$ . The former formula is been preferred throughout this work.

Fig. 1c shows the XRD patterns of solid phases recovered from solubility samples equilibrated in the presence of both  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  and  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$ . After terminating the solubility experiments in 0.51, 2.64 and 5.61 mol  $\text{kg}_w^{-1}$  NaCl ( $t = 80$  days), all reflections can be unequivocally attributed to either metaschoepite or sodium uranate. This indicates that the corresponding solution parameters ( $\text{pH}_m$  and [U]) are representative of the thermodynamic equilibrium between both solid phases.

### 3.1.1. Solubility measurements

Fig. 3 shows the experimental solubility data of  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  and  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$  determined in 0.03, 0.51, 2.64 and 5.61 mol  $\text{kg}_w^{-1}$  NaCl systems at  $\text{pH}_m = 4$ –14.5 (all data summarized

also as Supporting Information).  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  is the only solid phase controlling the solubility of U(VI) at  $\text{pH}_m$  below 6.5–8 (depending upon [NaCl]) in all investigated NaCl systems. Concentration of uranium in this pH region increases up to one order of magnitude with increasing ionic strength, expectedly due to ion interaction processes and complexation of U(VI) with chloride in concentrated NaCl systems. Changes in the slope of the solubility curve ( $\log [\text{U(VI)}]$  vs.  $\text{pH}_m$ ) with increasing ionic strength are related to changes in the aqueous speciation (i.e. ratio OH:U in the prevailing hydrolysis species) in equilibrium with  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$ . Solubility data of metaschoepite determined in the present work are in good agreement with previous solubility studies available in literature, mostly performed in dilute systems [3,8,11].

Solubility measurements in 0.03 mol  $\text{kg}_w^{-1}$  NaCl at  $\text{pH}_m = 9.5$ –11.5 with  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  as initial solid phase show a significant decrease in [U] with time. The concentration of uranium measured at short contact time ( $\approx 10^{-5}$  mol  $\text{kg}_w^{-1}$  at  $\text{pH}_m \approx 10$ ) agrees well with the high solubility expected for  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  under alkaline pH conditions. The significantly lower solubility measured after 140 days ( $10^{-6}$ – $10^{-6.5}$  mol  $\text{kg}_w^{-1}$ ) is indicative of a transformation process into  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$ , as confirmed by XRD (Fig. 1b).

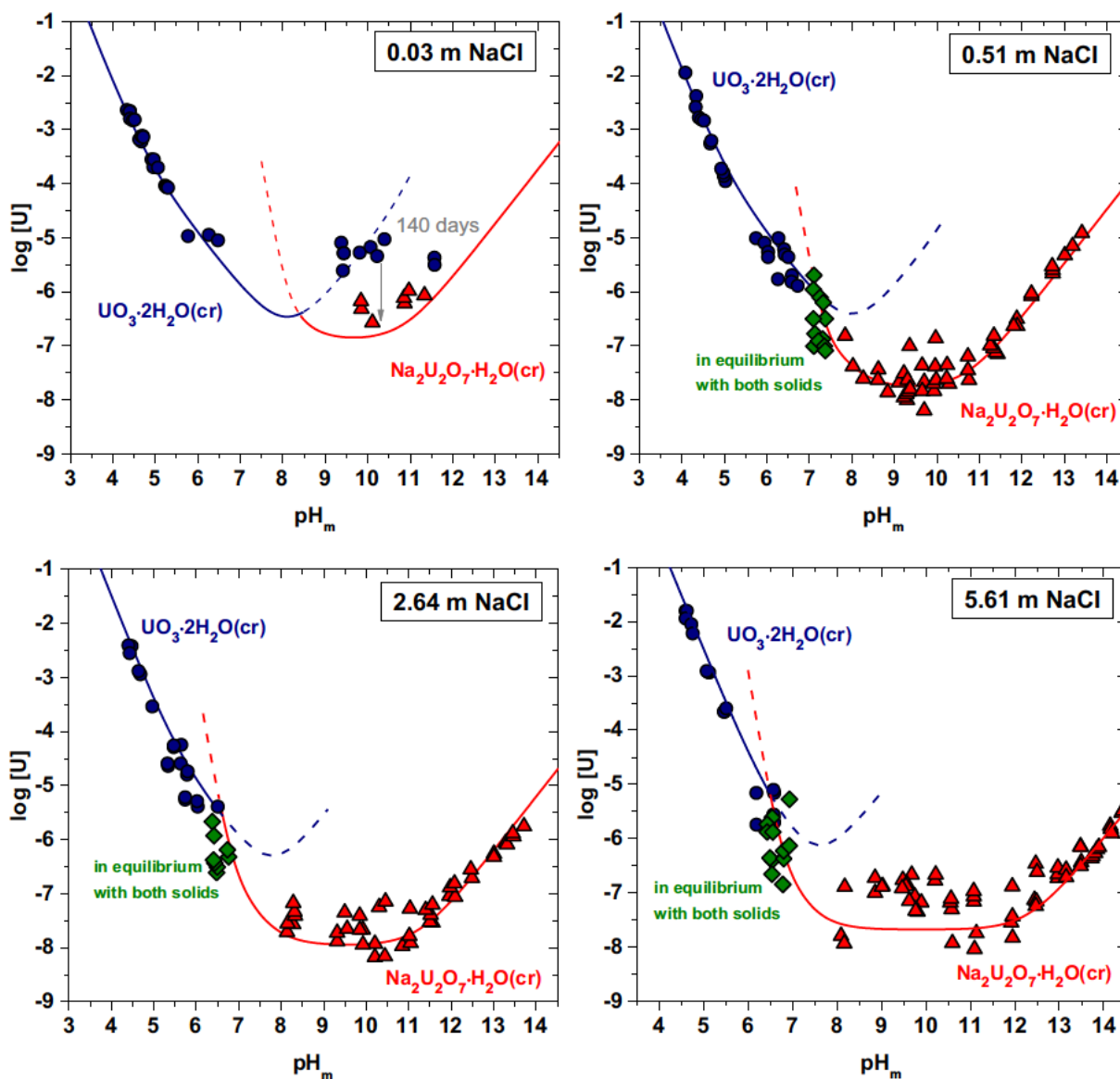


Fig. 3. Experimental solubility data of U(VI) in 0.03, 0.51, 2.64 and 5.61 mol kg<sup>-1</sup> NaCl solutions. Blue symbols: samples equilibrated with UO<sub>3</sub>·2H<sub>2</sub>O(cr); red symbols: samples equilibrated with Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr); green symbols: samples equilibrated with both UO<sub>3</sub>·2H<sub>2</sub>O(cr) and Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr). Solid lines are the calculated solubility with the thermodynamic and SIT activity models derived in the present study (see Tables 5 and 6). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Experimental Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr) solubility data gathered in 0.51, 2.64 and 5.61 mol kg<sup>-1</sup> NaCl systems at pH<sub>m</sub> = 8–14.5 are also shown in Fig. 3. Under weakly alkaline pH conditions, the solubility follows a pH independent behavior regardless of ionic strength. This agrees well with the equilibrium reaction  $0.5 \text{ Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{UO}_2(\text{OH})_3 + \text{Na}^+$ , which is consistent with the solid phase characterization performed in this work and aqueous speciation predicted with thermodynamic data selected in Ref. [2]. A slight decrease in [U(VI)] is observed in this pH region with increasing ionic strength, although experimental data points are scattered almost 1.5 orders of magnitude due to very low concentration of uranium, close to the detection limit of the measurement technique. At pH<sub>m</sub> above ≈ 11 (depending upon [NaCl]), the solubility of Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr) increases with a well defined slope of +1 (log [U] vs. pH<sub>m</sub>). This observation is consistent with a solubility control by the chemical equilibrium  $0.5 \text{ Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{UO}_2(\text{OH})_4^{2-} + \text{Na}^+ + \text{H}^+$ . In this pH region, the solubility of U(VI) decreases about one order of magnitude with increasing ionic

strength. A similar trend was reported in Ref. [33] for the solubility of Na<sub>2</sub>Np<sub>2</sub>O<sub>7</sub>(cr) in dilute to concentrated NaCl–NaOH solutions.

Solubility samples equilibrated in the presence of both solid phases (green symbols in Fig. 3) buffer the pH<sub>m</sub> at (7.22 ± 0.15), (6.43 ± 0.15) and (6.50 ± 0.15) in 0.51, 2.64 and 5.61 mol kg<sup>-1</sup> NaCl systems, respectively. Uranium concentrations measured for these systems provide a well defined and consistent transition between solubility data collected in acidic conditions in the presence of UO<sub>3</sub>·2H<sub>2</sub>O(cr), and [U] in equilibrium with Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr) measured under alkaline pH conditions.

### 3.1.2. Aqueous speciation: Titration and spectroscopic measurements

Titrations of supernatant solutions of selected samples were performed after terminating the solubility experiments in order to determine the OH:U ratio of the U(VI) species prevailing in solution. Differences between added HCl and measured [H<sup>+</sup>] (pH<sub>m</sub>) are attributed to the consumption of H<sup>+</sup> with the neutralization of OH groups in (UO<sub>2</sub>)<sub>x</sub>(OH)<sub>y</sub><sup>2x-y</sup> complexes. Table 1 summarizes experi

**Table 1**

Experimentally measured  $\log [U]$ ,  $\text{pH}_m$  and OH:U values determined with the titration of selected supernatant solutions with HCl. Experimental values are compared to OH:U ratios calculated for each  $\text{pH}_m$  using the aqueous speciation based on the thermodynamic and SIT activity models summarized in Tables 5 and 6.  $T = (22 \pm 2)^\circ\text{C}$ ,  $P = (1.01 \pm 0.01)$  bar.

Matrix	$\log [U]^a$	$\text{pH}_m^b$	OH:U (experimental)	Predominant species (calculated)	OH:U (calculated)
0.51 mol·kg <sub>w</sub> <sup>-1</sup> NaCl	-2.6	4.3	(0.62 ± 0.07)	(10), (22)	0.71
2.64 mol·kg <sub>w</sub> <sup>-1</sup> NaCl	-2.4	4.5	(0.96 ± 0.10)	(34), (10), (22)	0.86
5.61 mol·kg <sub>w</sub> <sup>-1</sup> NaCl	-1.9	4.7	(1.22 ± 0.15)	(34)	1.23

<sup>a,b</sup> ±0.05.

mentally measured  $[U(\text{VI})]$ ,  $\text{pH}_m$  and corresponding OH:U ratios determined in the titration experiments. The table indicates also the U(VI) aqueous species prevailing (> 20%) for each investigated salt system and  $\text{pH}_m$  value, as calculated with the thermodynamic and SIT activity models provided in Tables 5 and 6. The combination of  $\text{pH}_m$  and thermodynamically calculated aqueous speciation allows to determine an averaged OH:U ratio for each investigated sample, which can be compared with the experimental value.

Table 1 shows a very good agreement between experimental and calculated OH:U ratios, thus giving an additional experimental validation of the hydrolysis constants selected in Ref. [2] and SIT ion interaction coefficients derived in the present study (see Table 6). Results show that U(VI) speciation in acidic, concentrated NaCl solutions in equilibrium with  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  is dominated by the trimer  $(\text{UO}_2)_3(\text{OH})_4^{2+}$ . The relevant role of the (34) hydrolysis species in our concentrated chloride systems is consistent with previous e.m.f. measurements in 1.0 mol L<sup>-1</sup> NaCl [34] and 3.0 mol L<sup>-1</sup> NaCl [35]. Interestingly, the predominant hydrolysis species in concentrated media is strongly dependent on the background electrolyte, and thus the trimer (35) has been reported to prevail in concentrated nitrate and perchlorate solutions (see Ref. [1] and references therein). To explain such differences, Baes and Mesmer [36], Grenthe et al. [1] and more recently De Stefano et al. [22] discussed the possible formation of the ternary complex  $(\text{UO}_2)_3(\text{OH})_4\text{Cl}^+$  in concentrated chloride solutions, which would retain the same structure of the  $(\text{UO}_2)_3(\text{OH})_5^+$  (or  $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ ) trimer prevailing in non complexing media. All these studies concluded that the available data are insufficient to reach a firm conclusion on the nature of this species, and even less to provide an adequate parametrization of its thermodynamic quantities.

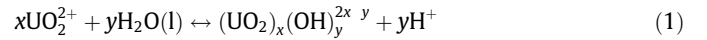
UV vis measurements performed before and after the titration experiments are shown in Fig. 4a and b, respectively. The strong absorption in the original solutions is consistent with the predominance of U(VI) polyatomic species. A very significant decrease in the absorption indicates that U(VI) monomeric species dominate after the titration to  $\text{pH}_m \approx 2$ . At this  $\text{pH}_m$ , the main U(VI) peak in 0.51 mol kg<sub>w</sub><sup>-1</sup> NaCl is observed at  $\lambda_{\text{max}} = 415$  nm with  $\epsilon = 9$  L mol<sup>-1</sup> cm<sup>-1</sup>, in moderate agreement with absorption data reported in the literature for  $\text{UO}_2^{2+}$  ( $\lambda_{\text{max}} = 413.9$  nm;  $\epsilon_{\text{max}} = 9.7 \pm 0.2$  L mol<sup>-1</sup> cm<sup>-1</sup>; [20]). The relevant red shift observed with increasing  $[\text{Cl}^-]$  ( $\lambda_{\text{max}} = 423$  nm in 5.61 mol kg<sub>w</sub><sup>-1</sup> NaCl, see Fig. 4b) can be attributed to the formation of inner sphere  $\text{UO}_2\text{Cl}_n^{2-n}$  complexes [37]. Spectra of the original solutions in the 0.51, 2.64 and 5.61 mol kg<sub>w</sub><sup>-1</sup> NaCl show similar patterns but increasing (normalized) absorption, likely reflecting the decreasing fraction of  $\text{UO}_2^{2+}$  and  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  in favour of the trimeric  $(\text{UO}_2)_3(\text{OH})_4^{2+}$  species. This is excellent agreement with the increasing OH:U ratio experimentally measured in the titration experiments (see Table 1). A number of spectroscopic studies have previously investigated the absorption of U(VI) in weakly acidic solutions [18,20,38,39]. Most of these studies were conducted in dilute to concentrated NaClO<sub>4</sub> solutions, whereas no data is available in concentrated chloride media. Only Lubal and Havel [38] reported the spectroscopic properties of  $(\text{UO}_2)_3(\text{OH})_4^{2+}$  ( $\lambda_{\text{max}} = 426.0 \pm 0.3$  nm;  $\epsilon_{\text{max}} = 52.4 \pm 0.6$  L mol<sup>-1</sup> cm<sup>-1</sup>). The value of  $\lambda_{\text{max}}$  provided by these authors is significantly lower than the

wavelength of the main peak observed in the present work (431–434 nm). Note however that the minor fraction of the (34) hydrolysis species in the experimental conditions of [38] (< 20%, 3.0 mol L<sup>-1</sup> NaClO<sub>4</sub>) and the intricate peak deconvolution required make difficult any accurate comparison for this species. Somehow discrepant data are available in the literature on the spectroscopic properties of  $(\text{UO}_2)_2(\text{OH})_2^{2+}$ :  $\lambda_{\text{max}} = 421.8$  nm,  $\epsilon_{\text{max}} = 101 \pm 2$  L mol<sup>-1</sup> cm<sup>-1</sup> [20] and  $\lambda_{\text{max}} = 419.3 \pm 0.2$  nm,  $\epsilon_{\text{max}} = 55.6 \pm 0.2$  L mol<sup>-1</sup> cm<sup>-1</sup> [38]. These values are consistent with the presence of  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  in the supernatant solutions investigated spectroscopically in the present study. It is out of the scope of this work to provide a quantitative evaluation of the spectroscopic data collected, but the results discussed above are in line with titration experiments and calculations conducted using thermodynamic data summarized in Tables 5 and 6.

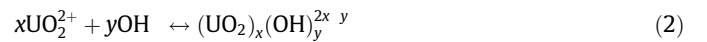
## 4. Chemical, thermodynamic and activity models

### 4.1. Definitions and terminology

The hydrolysis reactions of the  $\text{UO}_2^{2+}$  ion, i.e. the formation of U(VI) hydroxide complexes which are defined by the abbreviation  $(xy) = (\text{UO}_2)_x(\text{OH})_y^{2x-y}$ , are usually written as



or



The hydrolysis constants  ${}^*\beta'_{(x,y)}$  (in a given medium) and  ${}^*\beta^\circ_{(x,y)}$  (at infinite dilution), and the corresponding formation constants  $\beta'_{(x,y)}$  and  $\beta^\circ_{(x,y)}$  are defined by

$${}^*\beta'_{(x,y)} = \frac{[(\text{UO}_2)_x(\text{OH})_y^{2x-y}][\text{H}^+]^y}{[\text{UO}_2^{2+}]^x} \quad (3)$$

$${}^*\beta^\circ_{(x,y)} = \frac{{}^*\beta'_{(x,y)}(\gamma_{(x,y)})(\gamma_{\text{H}^+})^y}{(\gamma_{(1,0)})^x(a_w)^y} \quad (4)$$

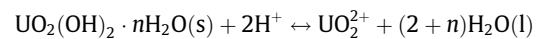
and

$$\beta'_{(x,y)} = \frac{[(\text{UO}_2)_x(\text{OH})_y^{2x-y}][\text{OH}^-]^y}{[\text{UO}_2^{2+}]^x[\text{OH}^-]^y} \quad (5)$$

$$\beta^\circ_{(x,y)} = \frac{\beta'_{(x,y)}(\gamma_{(x,y)})}{(\gamma_{(1,0)})^x(\gamma_{\text{OH}^-})^y} \quad (6)$$

respectively.  $[i]$  denotes the concentration of species  $i$ ,  $\gamma_i$  its activity coefficient and  $a_w$  the activity of water. The hydrolysis constants  $\log {}^*\beta^\circ_{(x,y)}$  are related to  $\log \beta^\circ_{(x,y)}$  by the ion product of water.

The solubility products of an U(VI) hydroxide/oxide  $\text{UO}_2(\text{OH})_2 \cdot n\text{H}_2\text{O}(\text{s})$ , ( ${}^*K^\circ_{s,0}$  at  $I = 0$  and  ${}^*K'_{s,0}$  in a given medium) are defined according to the dissolution equilibrium



$$\text{with } {}^*K'_{s,0} = \frac{[\text{UO}_2^{2+}][\text{H}^+]^2}{\quad} \quad (7)$$

$$\text{and } {}^*K^\circ_{s,0} = \frac{K'_{s,0}(\gamma_{\text{UO}_2^{2+}})(\gamma_{\text{H}^+})^2}{(a_w)^{(2+n)}} \quad (8)$$

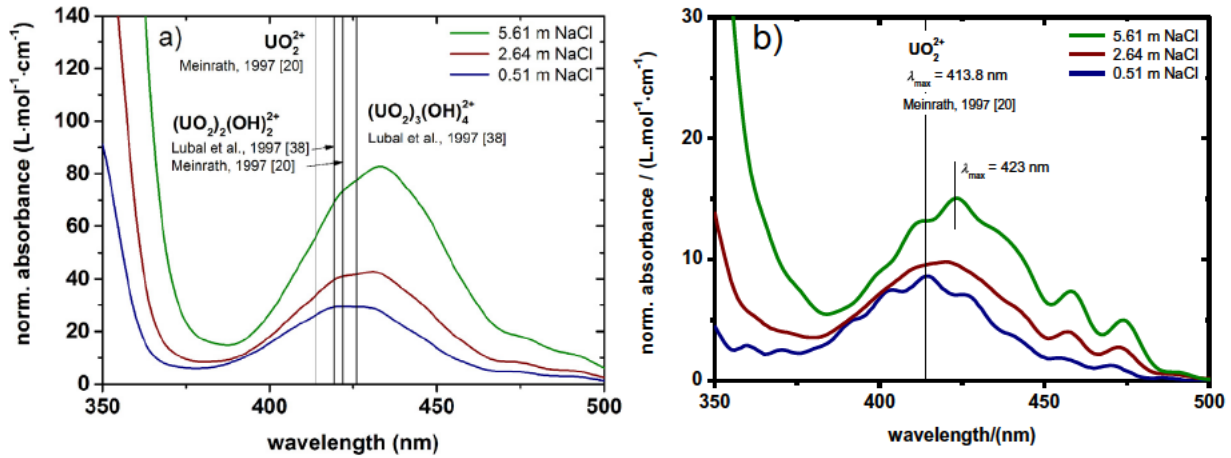


Fig. 4. Normalized UV-vis spectra of selected samples before (a) and after (b) titration to  $\text{pH}_m \approx 2$ . Concentration of U(VI) after ultrafiltration with 200 nm filters and  $\text{pH}_m$  before titration with HCl are summarized in Table 1. Reference spectroscopic data reported in the literature for  $\text{UO}_2^{2+}$ ,  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  and  $(\text{UO}_2)_3(\text{OH})_4^{2+}$  are appended to the figure for comparison purposes.

If there are no complexes with other inorganic ligands present in solution, the total metal concentration is given by

$$[\text{UO}_2^{2+}]_{\text{tot}} = [\text{UO}_2^{2+}] + \sum x[(\text{UO}_2)_x(\text{OH})_y^{2x-y}] + K'_{s,0}[\text{H}^+]^2 + \sum x(K'_{s,0}[\text{H}^+]^2)^x (\beta'_{(x,y)}[\text{H}^+]^{-y}) \quad (9)$$

The specific ion interaction theory (SIT) [40] has been considered in this work to calculate the activity coefficients of the ionic species present in solution. The SIT approach is also adapted in NEA TDB for the calculation of activity coefficients. According to the SIT, the conditional equilibrium constant  $\log^*K'$  is related to  $\log^*K^\circ$  at  $I = 0$  by

$$\log^*K' = \log^*K^\circ + \Delta z^2 D \Delta \varepsilon \cdot [X] + (2+n) \log a_w \quad (10)$$

with  $\Delta z^2 = \sum z^2(\text{products}) - \sum z^2(\text{educts})$  and  $\Delta \varepsilon = \sum \varepsilon_{ij}(\text{products}) - \sum \varepsilon_{ij}(\text{educts})$ ;  $z_i$  is the charge of ion  $i$ ,  $D$  is the Debye-Hückel term at 25 °C,  $D = 0.509 \sqrt{I_m} / (1 + \text{Ba}_i \sqrt{I_m})$ , with  $\text{Ba}_i = 1.5$ .  $[X]$  is the concentration (in molal units) of the counter ion in the background electrolyte<sup>\*</sup>, and  $\varepsilon_{ij}$  is the interaction parameter for a pair of oppositely charged ions. The so called "SIT plot" provides a linear regression of  $(\log^*K' - \Delta z^2 D + (2+n) \log a_w)$  vs.  $[X]$ , where the terms  $\Delta \varepsilon$  and  $\log^*K^\circ$  can be determined as slope and intercept, respectively. The applicability of SIT is normally limited to  $I_m \leq 3.5$  m, although recent studies conducted in our research group have also shown satisfactory results in concentrated NaCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> solutions with  $I_m$  up to  $\approx 15$  mol kg<sup>-1</sup> [31, 33, 41, 42].

#### 4.2. Thermodynamic data and SIT activity models for U(VI) hydrolysis species forming in acidic to near neutral pH conditions

As the speciation in saturated U(VI) solutions under the present conditions is always dominated by hydroxide complexes, the calculation of the solubility product of  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  is directly correlated with the hydrolysis constants. Slope analysis (as  $\log [\text{U(VI)}]$  vs.  $\text{pH}_m$ ) in solubility studies cannot distinguish between contributions from monomeric and oligomeric species of the same charge, e.g. from (10), (22) and (34), from (11), (35) and (47) or from (13) and (37). Therefore, the hydrolysis constants used in the present study for the complexes (11), (12), (22), (34), (35), (37) and (47) are adopted from the NEA TDB review [2] (see Table 2). A number of potentiometric studies published since 2002 [22-27] have reported thermodynamic data for the complexes (11), (22), (34)

and (35) in excellent agreement with the selection in [2]. Some of these studies [22, 24, 26, 27] provide also very similar hydrolysis constants for the anionic (37) complex, which however significantly differ from the thermodynamic selection in Ref. [2]. In combination with thermodynamic data selected in the NEA TDB for the complexes (11), (12), (22), (34), (35) and (47), the use of  $\log \beta^\circ_{(3,7)}$  reported in the most recent potentiometric studies results in a significant overestimation of our solubility data under weakly alkaline conditions. Note that the complex (37) forms in the pH region 6-9 with a low U(VI) solubility imposed by metaschoepite (or M uranates in M containing systems, with M = Li, Na, K, among others). Provided the high uranium concentrations used in the potentiometric studies in [22, 24, 26] ( $5 \cdot 10^{-4}$  to  $0.05$  mol L<sup>-1</sup>, 2-5 orders of magnitude oversaturated with respect to  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  at pH = 6-9, see Fig. 3), we consider the thermodynamic data derived from these studies unreliable for the complex (37). Zanonato and co workers [27] investigated the formation of the (37) complex (among others) in alkaline TMA NO<sub>3</sub> solutions. Although the study provides very relevant information on the aqueous speciation of U(VI) in this media, the ill defined interaction of TMA<sup>+</sup> with anionic species like  $(\text{UO}_2)_3(\text{OH})_7^{2-}$  prevents the selection of the  $\log \beta^\circ_{(3,7)}$  derived by these authors. Based on the discussion above, we have retained the NEA TDB selection for the (37) complex noting however that this species plays only a minor role in our experimental conditions. The complex  $(\text{UO}_2)_2\text{OH}^{3+}$  with the rather uncertain formation constant of  $\log^* \beta^\circ_{(2,1)} = (2.7 \pm 1.0)$  [1] is not included in the present calculations. The fraction of this complex becomes significant only at low ionic strength and total U(VI) concentrations above  $10^{-2}$  mol L<sup>-1</sup>, i.e. under conditions which are not relevant in the present study. Moreover, this complex was not included in speciation schemes derived from potentiometric titration data at higher ionic strength and hence also disregarded in the review of Brown [21].

The SIT coefficients  $\varepsilon((\text{UO}_2)_x(\text{OH})_y^{2x-y}, \text{Cl}^-)$  given in the NEA TDB [1] were derived accounting for the formation of the binary complexes  $\text{UO}_2\text{Cl}^+$  and  $\text{UO}_2\text{Cl}_2(\text{aq})$ , and assuming ion interaction coefficients of  $\text{UO}_2^{2+}$  and U(VI) hydrolysis species with Cl<sup>-</sup> to be the same as with ClO<sub>4</sub><sup>-</sup>. The later assumption is in our view incorrect and must be revisited. Furthermore, it cannot be ruled out that the proposed hydroxide complexes in concentrated NaCl solutions are also affected by additional complexation with chloride, although the data available in concentrated NaCl solutions are not sufficient for a parameterization of the ternary system U(VI)-OH-Cl.

\* Note that  $[\text{M}] = [\text{X}] = I_m$  in 1:1 MX electrolytes (e.g. NaCl)

**Table 2**

Hydrolysis constants<sup>a</sup> at  $I = 0$  and 25 °C, and SIT ion interaction coefficients ( $\epsilon(i,j)$ ) selected in the NEA-TDB update volume [2] for the U(VI) hydrolysis species forming under acidic to near-neutral pH conditions.

Species, $i$	( $xy$ )	$\log^* \beta^{\circ}_{(xy)}$	$j$	$\epsilon(i, j)$ [kg·mol <sup>-1</sup> ]
UO <sub>2</sub> OH <sup>+</sup>	(11)	$-5.25 \pm 0.24$	Cl	$(0.46 \pm 0.03)$
UO <sub>2</sub> (OH) <sub>2</sub> (aq)	(12)	$-12.15 \pm 0.17$		
(UO <sub>2</sub> ) <sub>2</sub> OH <sup>3+</sup>	(21)	$-2.7 \pm 1.0$		
(UO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup>	(22)	$-5.62 \pm 0.04$	Cl	$(0.69 \pm 0.07)$
(UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>	(34)	$-11.90 \pm 0.30$	Cl	$(0.50 \pm 0.18)$
(UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>5</sub> <sup>+</sup>	(35)	$-15.55 \pm 0.12$	Cl	$(0.81 \pm 0.17)$
(UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>7</sub> <sup>+</sup>	(37)	$-32.20 \pm 0.80$		
(UO <sub>2</sub> ) <sub>4</sub> (OH) <sub>7</sub> <sup>+</sup>	(47)	$-21.9 \pm 1.0$		

<sup>a</sup>  $\log^* \beta^{\circ}_{(xy)}$  for the reactions:  $x \text{UO}_2^{2+} + y \text{H}_2\text{O}(\text{l}) \rightleftharpoons (\text{UO}_2)_x(\text{OH})_y^{2x-y} + y \text{H}^+$ .

Consequently, we have preferred a thermodynamic model treating chloride complexation as strong ion ion interaction, i.e., by including this effect for both UO<sub>2</sub><sup>2+</sup> and (UO<sub>2</sub>)<sub>x</sub>(OH)<sub>y</sub><sup>2x-y</sup> complexes in the ion interaction coefficients of the SIT or Pitzer approaches. For this reason the SIT coefficients  $\epsilon((\text{UO}_2)_2(\text{OH})_2^{2+}, \text{Cl}) = (0.30 \pm 0.06)$  kg mol<sup>-1</sup>,  $\epsilon((\text{UO}_2)_3(\text{OH})_4^{2+}, \text{Cl}) = (0.07 \pm 0.17)$  kg mol<sup>-1</sup>,  $\epsilon((\text{UO}_2)_3(\text{OH})_5^+, \text{Cl}) = (0.24 \pm 0.15)$  kg mol<sup>-1</sup> and  $\epsilon((\text{UO}_2)_4(\text{OH})_7^+, \text{Cl}) = (0.17 \pm 0.18)$  kg mol<sup>-1</sup> are calculated in the present study directly from the original (uncorrected) equilibrium constants in dilute to concentrated NaCl solutions reported in [22,34,35], in combination with  $\epsilon(\text{UO}_2^{2+}, \text{Cl}) = (0.21 \pm 0.02)$  kg mol<sup>-1</sup> determined in [40] disregarding the formation of binary U(VI) Cl complexes, and the U(VI) hydrolysis constants selected in [2]. The SIT regressions for these species are shown in Fig. 5. The value of  $\epsilon(\text{UO}_2\text{OH}^+, \text{Cl}) = (0.10 \pm 0.10)$  kg mol<sup>-1</sup> is estimated based on typical values for the corresponding valence type, whereas we have assumed  $\epsilon(\text{UO}_2)_3(\text{OH})_7^+, \text{Na}^+) = \epsilon(\text{UO}_2)_3(\text{OH})_5^+, \text{Na}^+) = (0.24 \pm 0.09)$  kg mol<sup>-1</sup> according with the value for  $\epsilon(\text{UO}_2)_3(\text{OH})_3^+, \text{Na}^+)$  determined experimentally in this work. All SIT ion interaction coefficients derived or estimated in this work are summarized in Table 6.

#### 4.3. Evaluation of solubility products of UO<sub>3</sub>·2H<sub>2</sub>O(cr) and Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr)

Solubility products of UO<sub>3</sub>·2H<sub>2</sub>O(cr) and Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr) are evaluated in the present study based on the newly generated experimental solubility data. Conditional solubility products of UO<sub>3</sub>·2H<sub>2</sub>O(cr) are calculated according to Eq. (9) using experimental solubility data determined in 0.03, 0.51, 2.64 and 5.61 mol kg<sup>-1</sup> NaCl ( $4 \leq \text{pH}_m \leq 7$ ). Conditional hydrolysis constants at  $I_m$  required to solve equation (9) are calculated with  $\log^* \beta^{\circ}_{(xy)}$  selected in the NEA TDB (see Table 5) and SIT ion interaction coefficients derived in this work (see Table 6). Extrapolation of  $\log^* K'_{s,0}\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\}$  to  $I = 0$  is conducted using the SIT linear regression shown in Fig. 6, resulting in

$$\log^* K'_{s,0}\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\} = (5.35 \pm 0.13) \quad (11)$$

This value is considerably greater than  $\log^* K'_{s,0}\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\} = (4.8 \pm 0.43)$  selected in the NEA TDB [1,2], which resulted from the internal calculation with  $\Delta_f H^\circ_m$  and  $S^\circ_m$  determined in thermochemical studies [43–46]. The later studies used a highly crystalline UO<sub>3</sub>·2H<sub>2</sub>O(cr) material, obtained by the hydration of anhydrous UO<sub>3</sub>(cr) synthesized at  $T = 500$ – $600$  °C. Note that the solubility product determined in the present study is in very good agreement with  $\log^* K'_{s,0}\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\}$  reported in a number of solubility studies conducted at  $T = 20$ – $25$  °C [3,5–12]. The solubility product determined in the present work should therefore be used in thermodynamic/geochemical calculations involving UO<sub>3</sub>·2H<sub>2</sub>O(cr) precipitated at low temperatures. The use

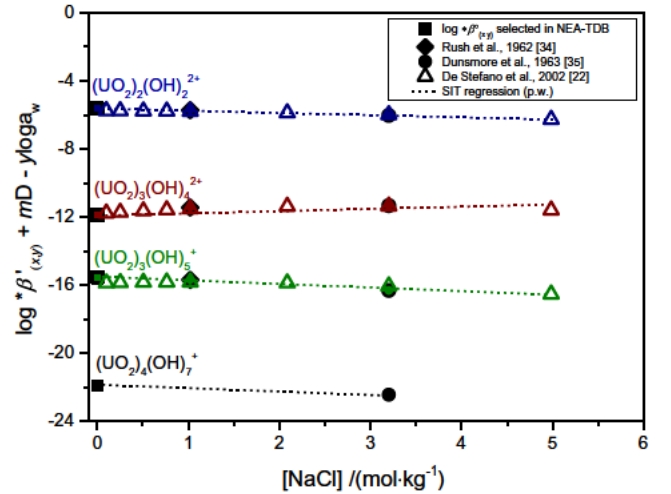


Fig. 5. SIT regression plot for the cationic (22), (34), (35), (47) hydroxide complexes, calculated using the uncorrected conditional constants previously reported for these species in dilute to concentrated NaCl solutions [22,34,35]. Values of  $\log^* \beta^{\circ}_{(xy)}$  are fixed in the fit with the corresponding hydrolysis constant selected in Ref. [2]. The uncertainties of the  $\log^* \beta^{\circ}_{(xy)}$  values are as small as the size of the symbols.

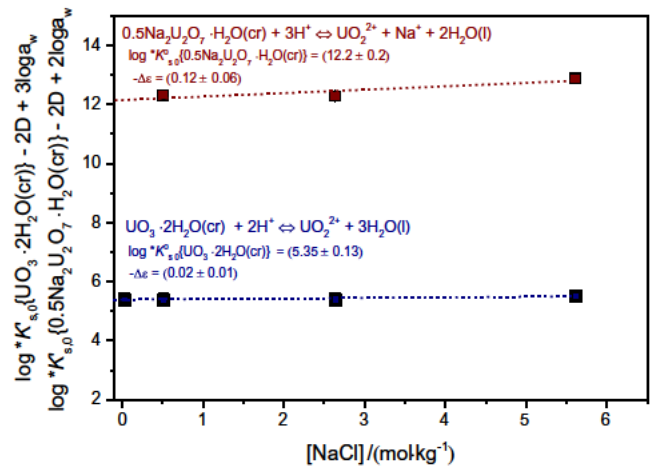


Fig. 6. SIT regression plot for the solubility product of UO<sub>3</sub>·2H<sub>2</sub>O(cr) and Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr) considering experimental  $\log^* K'_{s,0}\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\}$  and  $\log^* K'_{s,0}\{0.5\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\}$  obtained in NaCl systems.

of  $\log^* K'_{s,0}\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\}$  currently selected in the NEA TDB for the evaluation of these systems can lead to the underestimation of  $[\text{U(VI)}]_{\text{tot}}$ .

The solubility product of Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr) was evaluated using the equilibrium pH<sub>m</sub> for which the transformation of UO<sub>3</sub>·2H<sub>2</sub>O(cr) into Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr) takes place at a given NaCl concentration.

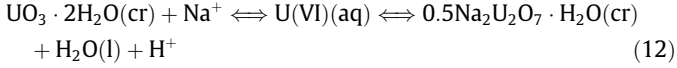


**Table 3**

Values of  $\text{pH}_m$  for the transition  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  and  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$ , and values of  $\log^* K'_{s,0}\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\}$  and  $\log^* K'_{s,0}\{0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\}$  calculated at  $I_m = 0.51, 2.64$  and  $5.61 \text{ mol} \cdot \text{kg}_w^{-1}$ ,  $T = (22 \pm 2)^\circ\text{C}$ ,  $P = (1.01 \pm 0.01) \text{ bar}$ .

Matrix	$\text{pH}_m$	$\log^* K'_{s,0}\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\}$	$\log^* K'_{s,0}\{0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\}$
$0.51 \text{ mol} \cdot \text{kg}_w^{-1} \text{ NaCl}$	$(7.22 \pm 0.15)$	$(5.76 \pm 0.13)$	$(12.69 \pm 0.15)$
$2.64 \text{ mol} \cdot \text{kg}_w^{-1} \text{ NaCl}$	$(6.43 \pm 0.15)$	$(6.00 \pm 0.13)$	$(12.85 \pm 0.15)$
$5.61 \text{ mol} \cdot \text{kg}_w^{-1} \text{ NaCl}$	$(6.50 \pm 0.15)$	$(6.5 \pm 0.13)$	$(13.62 \pm 0.15)$

Provided that  $\log^* K'_{s,0}\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\}$  is properly known,  $\log^* K'_{s,0}\{0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\}$  can be determined independently of U(VI) aqueous speciation according with:



$$\log^* K'_{s,0}\{0.5\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\} = \log^* K'_{s,0}\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\} + \log[\text{Na}^+] + \text{pH}_m \quad (13)$$

Following the Gibbs phase rule, the co existence of both U(VI) solid phases for a given  $[\text{NaCl}]$  is attained for an invariant point with constant  $[\text{H}^+]$  and  $[\text{U(VI)}]_{\text{tot}}$ . A large uncertainty for these quantities is experimentally measured in the solubility systems with both solid phases (green symbols in Fig. 1), very likely as a result of the similar and very low values of  $[\text{H}^+]$  and  $[\text{U(VI)}]_{\text{tot}}$  ( $10^{-6}$ – $10^{-7} \text{ mol kg}_w^{-1}$ ) at the transition  $\text{pH}_m$ . For this reason, we have determined the transition  $\text{pH}_m$  as the border between solubility experiments with  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  (blue symbols in Fig. 1), and those with co existence of  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  and  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$  as confirmed by XRD. Table 3 summarizes these  $\text{pH}_m$  values, together with  $\log^* K'_{s,0}\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\}$  at  $I_m = 0.51, 2.64$  and  $5.61 \text{ mol kg}_w^{-1} \text{ NaCl}$  calculated by SIT using  $\varepsilon(\text{UO}_2^{2+}, \text{Cl}^-) = (0.21 \pm 0.02) \text{ kg mol}^{-1}$  and  $\varepsilon(\text{H}^+, \text{Cl}^-) = (0.12 \pm 0.01) \text{ kg mol}^{-1}$ . The values of  $\log^* K'_{s,0}\{0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\}$  reported in the table are calculated according to Eq. (13).

The values of  $\log^* K'_{s,0}\{0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\}$  determined at  $I_m = 0.51, 2.64$  and  $5.61 \text{ mol kg}_w^{-1} \text{ NaCl}$  are extrapolated to  $I = 0$  using the SIT linear regression in Fig. 6, resulting in

$$\log^* K'_{s,0}\{0.5\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\} = (12.2 \pm 0.2) \quad (14)$$

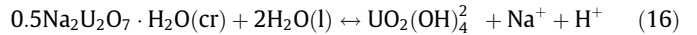
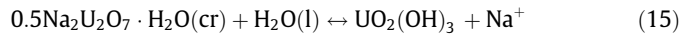
The values of  $\Delta\varepsilon\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr}), \text{UO}_2^{2+}\} = (0.02 \pm 0.01) \text{ kg mol}^{-1}$  and  $\Delta\varepsilon\{\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr}), \text{UO}_2^{2+}\} = (0.12 \pm 0.06) \text{ kg mol}^{-1}$  determined in the SIT plots in Fig. 6 are in excellent agreement with  $\Delta\varepsilon\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr}), \text{UO}_2^{2+}\} = \varepsilon(\text{UO}_2^{2+}, \text{Cl}^-) - 2 \varepsilon(\text{H}^+, \text{Cl}^-) = (0.03 \pm 0.04) \text{ kg mol}^{-1}$  and  $\Delta\varepsilon\{\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr}), \text{UO}_2^{2+}\} = \varepsilon(\text{UO}_2^{2+}, \text{Cl}^-) + 3 \varepsilon(\text{H}^+, \text{Cl}^-) = (0.12 \pm 0.04) \text{ kg mol}^{-1}$  calculated using  $\varepsilon(\text{UO}_2^{2+}, \text{Cl}^-) = (0.21 \pm 0.02) \text{ kg mol}^{-1}$ ,  $\varepsilon(\text{Na}^+, \text{Cl}^-) = (0.03 \pm 0.01) \text{ kg mol}^{-1}$  and  $\varepsilon(\text{H}^+, \text{Cl}^-) = (0.12 \pm 0.01) \text{ kg mol}^{-1}$  as reported in Refs. [40,2]. This agreement provides an additional validation of the approach used for the determination of  $\log^* K'_{s,0}\{\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\}$  and  $\log^* K'_{s,0}\{0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\}$ .

The value of  $\log^* K'_{s,0}\{0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\}$  determined in the present work is considerably greater than the solubility product calculated internally from  $\Delta_r H^\circ_m$  and  $S^\circ_m$  selected in the NEA TDB [2] for the anhydrous phase,  $\log^* K'_{s,0}\{0.5 \text{Na}_2\text{U}_2\text{O}_7(\text{cr})\} = (11.3 \pm 0.5)$ . Note again that enthalpy and entropy values selected in [2] were determined for a very crystalline phase synthesized at  $T = 700$ – $1000^\circ\text{C}$  [47,48], and thus discrepancies in  $\log^* K'_{s,0}$  can be properly rationalized by differences in the particle size of  $\text{Na}_2\text{U}_2\text{O}_7(\text{cr})$  [47,48] and  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$  (p.w.). Yamamura and co workers investigated the solubility of  $\text{Na}_2\text{U}_2\text{O}_7 \cdot x\text{H}_2\text{O}(\text{cr})$  at  $T = (25 \pm 1)^\circ\text{C}$  under alkaline carbonate solutions [13]. The authors determined a solubility constant for the equilibrium reaction  $0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot x\text{H}_2\text{O}(\text{cr}) + 3 \text{CO}_3^{2-} + (1.5 - x) \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{UO}_2(\text{CO}_3)_3^{4-} + 3 \text{OH}^- + \text{Na}^+$ , which combined with  $\log^* K^\circ\{\text{UO}_2(\text{CO}_3)_3^{4-}\} = (21.84 \pm 0.04)$  selected in

Ref. [2] results in  $\log^* K'_{s,0}\{0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\} = (29.7 \pm 1.0)$  ( $\log^* K'_{s,0}\{0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\} = (12.3 \pm 1.0)$ ). Although with a very large uncertainty, this value is in excellent agreement with  $\log^* K'_{s,0}\{0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\}$  determined in the present study. On the contrary, our  $\log^* K'_{s,0}\{0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\}$  is in large disagreement with the solubility product reported by Gorman Lewis and co workers [12] for the analogous phase clarkeite,  $\log^* K'_{s,0}\{\text{Na}(\text{UO}_2)\text{O}(\text{OH})(\text{cr})\} = 9.4 (0.9/+0.6)$ . The latter value is also significantly lower than  $\log^* K'_{s,0}$  calculated from thermodynamic quantities selected in the NEA TDB for the anhydrous, highly crystalline  $\text{Na}_2\text{U}_2\text{O}_7(\text{cr})$  phase. A close inspection of the experimental results in Ref. [12] shows that the solubility product of the Na uranate formulated as  $\text{Na}(\text{UO}_2)\text{O}(\text{OH})(\text{cr})$  was calculated from experiments performed in  $0.1 \text{ mol L}^{-1} \text{ NaNO}_3$  at  $4.3 \leq \text{pH} \leq 6.3$ . According to our experimental results in Fig. 3,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  is the solid phase controlling the solubility of U(VI) under these experimental conditions, and indeed, Gorman Lewis et al. reported the presence of  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  after terminating all their solubility experiments with  $\text{Na}(\text{UO}_2)\text{O}(\text{OH})(\text{cr})$ . In our view, these shortcomings invalidate the approach in [12] for an accurate quantification of  $\log^* K'_{s,0}\{\text{Na}(\text{UO}_2)\text{O}(\text{OH})(\text{cr})\}$ .

#### 4.4. Thermodynamic and SIT activity models for U(VI) hydrolysis species forming in alkaline to hyperalkaline pH conditions

U(VI) solubility in dilute to concentrated NaCl solutions shows two well defined regions in the alkaline pH range: (i) pH independent solubility behavior at  $8 \leq \text{pH}_m \leq 11$ , and (ii) increase in solubility with a well defined slope of +1 at  $\text{pH}_m > 11$ . Considering a solubility control by  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$ , these observations are properly explained by the predominance of the species  $\text{UO}_2(\text{OH})_3$  and  $\text{UO}_2(\text{OH})_4^{2-}$  in the aqueous phase, respectively:



with

$$\log^* K'_{s,(1,3)} = \log[\text{UO}_2(\text{OH})_3] + \log[\text{Na}^+] \quad (17)$$

$$\log^* K'_{s,(1,3)} = \log^* K'_{s,(1,3)} + \log \gamma_{\text{UO}_2(\text{OH})_3} + \log \gamma_{\text{Na}^+} - \log a_w \quad (18)$$

and

$$\log^* K'_{s,(1,4)} = \log[\text{UO}_2(\text{OH})_4^{2-}] + \log[\text{Na}^+] + \log[\text{H}^+] \quad (19)$$

$$\log^* K'_{s,(1,4)} = \log^* K'_{s,(1,4)} + \log \gamma_{\text{UO}_2(\text{OH})_4^{2-}} + \log \gamma_{\text{Na}^+} + \log \gamma_{\text{H}^+} - 2 \log a_w \quad (20)$$

Conditional solubility constants  $\log^* K'_{s,(1,3)}$  and  $\log^* K'_{s,(1,4)}$  are determined according to Eqs. (15) and (17) on the basis of experimental solubility data in  $0.51, 2.64$  and  $5.61 \text{ mol kg}_w^{-1} \text{ NaCl}$ . These conditional constants are extrapolated to  $I = 0$  in the SIT regressions shown in Fig. 7, resulting in

$$\log^* K'_{s,(1,3)} = (8.5 \pm 0.4)$$

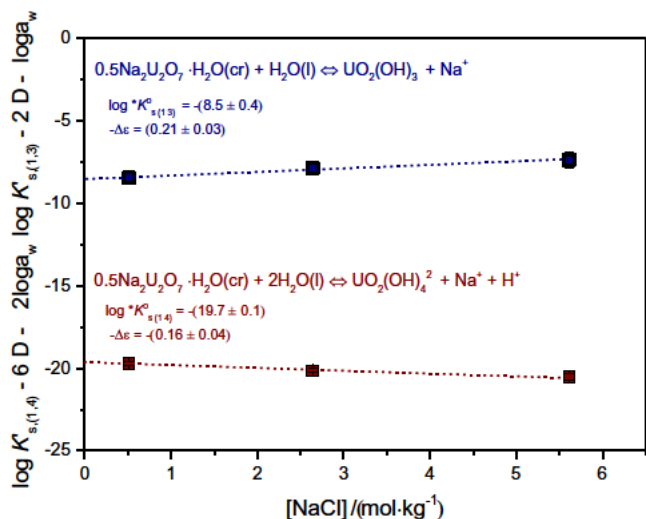


Fig. 7. Extrapolation of  $\log^* K_{s(1,3)}^{\circ}$  and  $\log^* K_{s(1,4)}^{\circ}$  determined in 0.51, 2.64 and 5.61 mol·kg<sup>-1</sup> NaCl to  $I=0$  using the SIT linear regression.

$$\log^* K_{s(1,4)}^{\circ} \quad (19.7 \pm 0.1)$$

Combining  $\log^* K_{s(1,3)}^{\circ}$  and  $\log^* K_{s(1,4)}^{\circ}$  with  $\log^* K_{s,0}^{\circ}\{0.5 \text{ Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})\}$  determined in the previous section, we obtain

$$\log^* \beta_{(1,3)}^{\circ} \quad (20.7 \pm 0.4)$$

$$\log^* \beta_{(1,4)}^{\circ} \quad (31.9 \pm 0.2)$$

SIT ion interaction coefficients of  $\text{UO}_2(\text{OH})_3$  and  $\text{UO}_2(\text{OH})_4^{2-}$  can be calculated from the slope of the corresponding SIT plot ( $\Delta\varepsilon = \varepsilon(\text{UO}_2(\text{OH})_3, \text{Na}^+) - \varepsilon(\text{Na}^+, \text{Cl}^-)$ , and  $\Delta\varepsilon = \varepsilon(\text{UO}_2(\text{OH})_4^{2-}, \text{Na}^+) - \varepsilon(\text{Na}^+, \text{Cl}^-) - \varepsilon(\text{H}^+, \text{Cl}^-)$ ), using  $\varepsilon(\text{Na}^+, \text{Cl}^-) = (0.03 \pm 0.01)$  kg mol<sup>-1</sup> and  $\varepsilon(\text{H}^+, \text{Cl}^-) = (0.12 \pm 0.01)$  kg mol<sup>-1</sup> as reported in [2]:

$$\varepsilon(\text{UO}_2(\text{OH})_3, \text{Na}^+) \quad (0.24 \pm 0.09) \text{ kg} \cdot \text{mol}^{-1}$$

$$\varepsilon(\text{UO}_2(\text{OH})_4^{2-}, \text{Na}^+) \quad (0.01 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}$$

Hydrolysis constants determined in the present study for  $\text{UO}_2(\text{OH})_3$  and  $\text{UO}_2(\text{OH})_4^{2-}$  are compared in Table 4 with thermodynamic data available in literature. The table includes also data reported in [33] for the analogous Np(VI) complexes,  $\text{NpO}_2(\text{OH})_3$  and  $\text{NpO}_2(\text{OH})_4^{2-}$ . The later values were derived in the context of

a solubility study with  $\text{Na}_2\text{Np}_2\text{O}_7(\text{cr})$  in dilute to concentrated NaCl NaOH solutions, under experimental conditions very similar to those considered in the present work.

Table 4 shows that  $\log^* \beta_{(1,3)}^{\circ}$  derived in the present work agrees within the uncertainties with data reported in previous solubility studies with U(VI) [4,13] and Np(VI) [33]. On the other hand, very significant deviations in  $\log^* \beta_{(1,3)}^{\circ}$  (almost 2 log<sub>10</sub> units) arise with the recent potentiometric study by Zanonato and co workers [27,28]. The later experiments were performed using TMA NO<sub>3</sub> as background electrolyte to avoid the precipitation of M(I) uranates (M(I) = Na, K, ...) at the high uranium concentrations used in the study ( $7 \cdot 10^4 \text{ mol L}^{-1} \leq [\text{U(VI)}]_0 \leq 2 \cdot 10^3 \text{ mol L}^{-1}$ ). Although acknowledging the validity of the approach in Refs. [27,28], several aspects can explain the large discrepancy with thermodynamic quantities derived for  $\text{UO}_2(\text{OH})_3$  in the present study. First, the very different range of U concentrations in [27,28] ( $7 \cdot 10^4 \text{ mol L}^{-1} \leq [\text{U(VI)}]_0 \leq 2 \cdot 10^3 \text{ mol L}^{-1}$ ) and the present study ( $10^7 \text{ mol L}^{-1} \leq [\text{U(VI)}]_0 \leq 10^8 \text{ mol L}^{-1}$ , in the pH range where  $\text{UO}_2(\text{OH})_3$  prevails) can likely lead to significant differences in the hydrolysis species prevailing in solution especially regarding formation of polyatomic species. Indeed, the authors reported also the formation and predominance of the complex  $(\text{UO}_2)_3(\text{OH})_8^{2-}$  within the same pH range as  $\text{UO}_2(\text{OH})_3$ . Second, the interaction of the very bulky cation TMA<sup>+</sup> with anionic species remains ill defined, and can be responsible of large differences with respect to thermodynamic data derived in NaCl media.

The SIT ion interaction coefficient determined in the present work for the (13) complex,  $\varepsilon(\text{UO}_2(\text{OH})_3, \text{Na}^+) = (0.24 \pm 0.09)$  kg mol<sup>-1</sup>, is in excellent agreement with  $\varepsilon(\text{NpO}_2(\text{OH})_3, \text{Na}^+) = (0.20 \pm 0.02)$  kg mol<sup>-1</sup> reported in Ref. [33], but differs significantly from the value reported in Ref. [13] ( $\varepsilon(\text{UO}_2(\text{OH})_3, \text{Na}^+) = (0.83 \pm 0.20)$  kg mol<sup>-1</sup>). The latter value is unexpectedly large for a species with charge -1. Note that Yamamura and co workers conducted their experiments in the presence of carbonate ( $2 \cdot 10^3 \text{ mol L}^{-1} \leq C_{\text{tot}} \leq 0.15 \text{ mol L}^{-1}$ ), and the co existence of  $\text{UO}_2(\text{OH})_3$  with the highly charged  $\text{UO}_2(\text{CO}_3)_3^{4-}$  complex has probably interfered in the accurate determination of  $\log^* \beta_{(1,3)}^{\circ}$  at elevated  $I$ , where the tricarbonato complex becomes predominant.

The value of  $\log^* \beta_{(1,4)}^{\circ}$  determined in the present work agrees within the uncertainties with thermodynamic data reported in Ref. [13], and is in excellent agreement with  $\log^* \beta_{(1,4)}^{\circ}$  reported in Ref. [33] for Np(VI). In contrast to the (13) complex, a moderate agreement is also obtained with thermodynamic data determined in the potentiometric study by Zanonato et al. [27,28]. This is possibly due to the greater solubility of  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$  in the pH range where the (14) complex prevails, and thus to the closer range

Table 4

Comparison of hydrolysis constants derived in the present work (p.w.) for  $\text{UO}_2(\text{OH})_3$  and  $\text{UO}_2(\text{OH})_4^{2-}$ , with data reported in the literature for the same species [2,4,13,28] and for the analogous Np(VI) complexes [33].  $P = (1.01 \pm 0.01)$  bar,  $T$  (°C) as indicated.

Element	Method	Medium	$T$ (°C)	$\log_{10}^* \beta_{(\alpha,\gamma)}^{\circ}$	References
U	Solubility	0.5 mol·L <sup>-1</sup> NaClO <sub>4</sub>	25	-(20.1 ± 0.5)	[4]
		0.5–3.0 mol·L <sup>-1</sup> NaClO <sub>4</sub> –NaHCO <sub>3</sub> –NaOH	(25 ± 1)	-(20.6 ± 1.1) <sup>a</sup>	[13]
	Review			-(20.25 ± 0.64)	[2]
	Potentiometry, calorimetry	0.1 mol·L <sup>-1</sup> TMA–NO <sub>3</sub>	25.00	-(18.81 ± 0.17) <sup>b</sup>	[27,28]
	Solubility	0.5–5.0 mol·L <sup>-1</sup> NaCl–NaOH	(22 ± 2)	-(20.7 ± 0.4)	(p.w.)
Np	Solubility	0.1–5.0 mol·L <sup>-1</sup> NaCl–NaOH	(22 ± 2)	-(21.2 ± 1.1)	[33]
U	Solubility	0.5–3.0 mol·L <sup>-1</sup> NaClO <sub>4</sub> –NaHCO <sub>3</sub> –NaOH	(25 ± 1)	-(32.1 ± 1.0) <sup>a</sup>	[13]
				-(32.4 ± 0.68)	[2]
	Potentiometry, calorimetry	0.1 mol·L <sup>-1</sup> TMA–NO <sub>3</sub>	25.00	-(31.25 ± 0.50) <sup>b</sup>	[27,28]
	Solubility	0.5–5.0 mol·L <sup>-1</sup> NaCl–NaOH	(22 ± 2)	-(31.9 ± 0.2)	(p.w.)
	Solubility	0.1–5.0 mol·L <sup>-1</sup> NaCl–NaOH	(22 ± 2)	-(32.0 ± 1.1)	[33]

<sup>a</sup> Recalculated in this work using  $\log^* K^{\circ}\{\text{UO}_2(\text{CO}_3)_3^{4-}\}$  selected in Ref. [2].

<sup>b</sup> Value in 0.1 mol·L<sup>-1</sup> TMA–NO<sub>3</sub>.

**Table 5**  
Solubility and hydrolysis constants at  $I = 0$  selected in the present work for the system  $U^{VI}$ - $Na^+$ - $H^+$ - $Cl^-$ - $OH^-$ - $H_2O(l)$ .  $P = (1.01 \pm 0.01)$  bar.

Solid phases	$\log^* K_{s,0}^{\circ}$	References	
$UO_3 \cdot 2H_2O(cr)$	$(5.35 \pm 0.13)$	(p.w.)	
$0.5 Na_2U_2O_7 \cdot H_2O(cr)$	$(12.2 \pm 0.2)$	(p.w.)	
Hydrolysis species	$(xy)$	$\log^* \beta_{(xy)}^{\circ}$	References
$UO_2OH^+$	(11)	$-(5.25 \pm 0.24)$	[2]
$UO_2(OH)_2(aq)$	(12)	$-(12.15 \pm 0.17)$	[2]
$UO_2(OH)_3$	(13)	$-(20.7 \pm 0.40)$	(p.w.)
$UO_2(OH)_4^+$	(14)	$-(31.9 \pm 0.2)$	(p.w.)
$(UO_2)_2(OH)_2^{2+}$	(22)	$-(5.62 \pm 0.04)$	[2]
$(UO_2)_3(OH)_4^{2+}$	(34)	$-(11.9 \pm 0.3)$	[2]
$(UO_2)_3(OH)_5^+$	(35)	$-(15.55 \pm 0.12)$	[2]
$(UO_2)_3(OH)_7$	(37)	$-(32.20 \pm 0.80)$	[2]
$(UO_2)_4(OH)_7^+$	(47)	$-(21.9 \pm 1.0)$	[2]

**Table 6**  
SIT ion interaction coefficients  $\varepsilon(i,j)$  for  $UO_2^{2+}$  and U(VI) hydrolysis species reported in Ref. [40] and derived in the present work from experimental data and estimation methods.  $P = (1.01 \pm 0.01)$  bar.

U(VI) species	SIT coefficients		References
$I$	$j$	$\varepsilon(i,j)$	
$UO_2^{2+}$	Cl	$(0.21 \pm 0.02)^a$	[40]
$UO_2OH^+$	Cl	$(0.10 \pm 0.10)^b$	(p.w.)
$(UO_2)_2(OH)_2^{2+}$	Cl	$(0.30 \pm 0.06)^c$	(p.w.)
$(UO_2)_3(OH)_4^{2+}$	Cl	$-(0.07 \pm 0.17)^c$	(p.w.)
$(UO_2)_3(OH)_5^+$	Cl	$(0.24 \pm 0.15)^c$	(p.w.)
$(UO_2)_4(OH)_7^+$	Cl	$(0.17 \pm 0.18)^c$	(p.w.)
$UO_2(OH)_3$	$Na^+$	$-(0.24 \pm 0.09)$	(p.w.)
$UO_2(OH)_4^+$	$Na^+$	$(0.01 \pm 0.04)$	(p.w.)
$(UO_2)_3(OH)_7$	$Na^+$	$-(0.24 \pm 0.09)^d$	(p.w.)
$UO_2(OH)_2(aq)$	$Na^+, Cl$	0	<sup>e</sup>

<sup>a</sup> This value given in [40] includes chloride complexation treated as strong ion-ion interaction.

<sup>b</sup> Estimated using the approach in Ref. [49] or from typical values for the corresponding valence type.

<sup>c</sup> Determined in the present work from potentiometric data reported elsewhere [22,34,35,50] considering chloride complexation as strong ion-ion interaction.

<sup>d</sup> Set equal to  $\varepsilon(UO_2(OH)_3, Na^+)$ .

<sup>e</sup> By definition in SIT.

of  $[U(VI)]$  used in both studies. The value of  $\varepsilon(UO_2(OH)_4^+, Na^+)$  determined in the present work is slightly more positive than those reported in Ref. [13] ( $\varepsilon(UO_2(OH)_4^+, Na^+) = (0.13 \pm 0.08)$  kg mol<sup>-1</sup>) and in Ref. [33] ( $\varepsilon(NpO_2(OH)_4^+, Na^+) = (0.12 \pm 0.01)$  kg mol<sup>-1</sup>).

#### 4.5. Summary of chemical, thermodynamic and activity models selected in the present study for the system $U^{VI}$ - $Na^+$ - $H^+$ - $Cl^-$ - $OH^-$ - $H_2O(l)$

Tables 5 and 6 summarize the chemical, thermodynamic and SIT activity models selected in the present work. The selection is based on the evaluation of own experimental data, the use of thermodynamic data selected in the NEA TDB and the application of empirical methods for the estimation of some ion interaction coefficients. Solubility curves calculated according to these models are compared in Fig. 3 with experimental data gathered in this work in NaCl systems.

## 5. Conclusions

Metaschoepite  $UO_3 \cdot 2H_2O(cr)$  and sodium uranate with the sum formula  $Na_2U_2O_7 \cdot H_2O(cr)$  or  $NaUO_2O(OH)(cr)$  are formed as stable, solubility limiting solid phases of U(VI) in 0.03–5.61 mol kg<sup>-1</sup> NaCl solutions at  $pH_m = 4–14$ . The solubility products determined in

the present work,  $\log^* K_{s,0}^{\circ}\{UO_3 \cdot 2H_2O(cr)\} = (5.35 \pm 0.13)$  and  $\log^* K_{s,0}^{\circ}\{0.5 Na_2U_2O_7 \cdot H_2O(cr)\} = (12.2 \pm 0.2)$  are consistent with data from previous solubility studies, but more accurate. They are also noticeably greater than the values calculated from the thermochemical data and standard molar Gibbs energies selected in the NEA TDB for highly crystalline phases synthesized at elevated temperatures (500–1000 °C).

Hydrolysis constants  $\log^* \beta_{(xy)}^{\circ}$  selected in the NEA TDB reviews [2003GUI/FAN] for the species  $(UO_2)_x(OH)_y^{2x-y}$  with  $(xy) = (11), (12), (13), (22), (34), (35), (37)$  and (47), in combination with SIT ion interaction coefficients derived in the present study are appropriate to model the solubility of U(VI) in acidic, dilute to concentrated NaCl solutions. Titration data and UV-vis absorption spectra obtained NaCl solutions saturated with  $UO_3 \cdot 2H_2O(cr)$  confirm the speciation predicted with this data set. The hydrolysis constants for the complexes  $UO_2(OH)_3$  and  $UO_2(OH)_4^+$ ,  $\log^* \beta_{(1,3)}^{\circ} = (20.7 \pm 0.4)$  and  $\log^* \beta_{(1,4)}^{\circ} = (31.9 \pm 0.2)$ , are derived from solubility experiments with  $Na_2U_2O_7 \cdot H_2O(cr)$  in alkaline NaCl solutions. These values agree within the uncertainties with the thermodynamic selection in NEA TDB, but represent an improved accuracy with respect to previous experimental studies.

This work provides chemical, thermodynamic and SIT activity models for the system  $U^{VI}$ - $Na^+$ - $H^+$ - $Cl^-$ - $OH^-$ - $H_2O(l)$ , and represents an accurate and robust tool for the calculation of U(VI) solubility in NaCl solutions relevant for nuclear waste disposal. To the best of our knowledge, it is the first time that this system is treated in such a comprehensive manner, models being valid for dilute to concentrated NaCl solutions and covering acidic to hyperalkaline pH conditions.

Based on the present work and experimental data in NaCl solutions and additional metaschoepite solubility studies in dilute to concentrated  $MgCl_2$  solutions not reported here, a comprehensive set of ion interaction coefficients for thermodynamic modelling with the thermodynamic Pitzer approach (for the description of highly saline solutions) will be presented in a following paper.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2017.05.039>.

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