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The solubility of $(UO_2)_3(PO_4)_2 \cdot 4H_2O(s)$ and the formation of U(VI) phosphate complexes: Their influence in uranium speciation in natural waters

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Abstract—Uranium is commonly associated in natural waters with O-containing ligands both in the aqueous and the solid phases. Phosphate is present in most of these systems; however, the thermodynamics of the U(VI)-H_3PO_4 system are poorly known, particularly in the pH range of interest 6 to 9. Hence, the effect of phosphate on the migration of uranium in natural waters is not well understood.

We have investigated the solubility of a well-characterized U(VI)-phosphate phase in the pH range 3 to 9: $(UO_2)_3(PO_4)_2 \cdot 4H_2O(s)$ Analysis of these data indicates the formation of the predominant species $UO_2HPO_4(aq)$ and $UO_2PO_4^-$ in the pH range 4–9. Their formation constants as well as the solubility constant of $(UO_2)_3(PO_4)_2 \cdot 4H_2O(s)$ have been determined. From the same experiments we have established the equilibrium constant of the hydroxide complex $UO_2(OH)_3^-$. A discussion of the hydrolysis of U(VI) is also reported.

The effect of phosphate on the mobility of U in natural waters is assessed in the light of these new data. They indicate that in the pH range of most natural waters, 6 to 9, U(VI) will be associated to aqueous phosphate complexes when the total concentration ratio $[PO_4^{3-}]_T/[CO_3^{2-}]_T$ is greater than 10^{-1}.

INTRODUCTION

TRACE ELEMENT MIGRATION and cycling is related to the cycling of major components through the different reservoirs. The migration of U in the geosphere is particularly linked to the C, P, Fe, and Si cycles.

The interaction between the U and P cycles in the geosphere involves both the solid state and aqueous solutions. Uranium (VI) is immobilized in many phosphate minerals (see Table 1). These extensively occur at the Kongarra deposit, located in the Alligator River Province in Australia (DUERDEN, 1990). These deposits are the result of the oxidation of the primary $UO_2(s)$ through the Fe cycling and their later precipitation as U(VI) phosphates. As a consequence, a correlation between the U and phosphate in the groundwaters has been suggested (DUERDEN, 1990). The same patterns of U/phosphate mineralization are found in the Southern Karoo (South Africa) and in the ore deposits of the Northwestern Province of Zambia (IAEA, 1981).

In the aqueous phase, U, as the other actinides, has a tendency to form strong complexes with O-containing ligands. Among these, hydroxide, carbonate, and phosphate are the ones most commonly found in natural waters. Much attention has been devoted to the understanding of the geochemical behaviour of U in the hydroxide and carbonate systems (BAES and MESMER, 1976; SYLVA and DAVIDSON, 1979; CIAVATTA et al., 1979, 1981; LEMIRE and TREMAINE, 1982; FERRI et al., 1981; MAYA, 1982; GRENTHE et al., 1984; BRUNO et al., 1986). LANGMUIR (1978) pointed out the potential importance of phosphate complexation in the U(VI) speciation in natural waters. However, his conclusions were based on erroneous U(VI)-phosphate speciation and the associated constants were overestimated (for a detailed discussion see TRIPATHI, 1983). Hence, there is no reliable information concerning the composition and stability of the U(VI)-phosphate complexes in the pH range 6 to 9.

The experimental studies in this system have been complicated by the formation of a number of sparingly soluble solid phases (SCHREYER and BAES, 1954) and the presence of a large variety of phosphate complexes. Under oxidizing conditions, $[PO_4^{3-}]_T < 0.014$ mol dm^{-3}, and low temperatures, the normal uranyl phosphate $(UO_2)_3(PO_4) \cdot 4H_2O(s)$ has been reported as the stable solid phase (SCHREYER and BAES, 1954). There are very few precise studies of its solubility available in the literature. Most of them refer to low-pH media and fairly high concentration of phosphoric acid (SCHREYER and BAES, 1954; KARPOV, 1961; VESELY et al., 1965). The most comprehensive study on the solubility of well-characterized uranyl orthophosphate, $(UO_2)_3(PO_4) \cdot 4H_2O(s)$, is that of VESELY et al., (1965). They reported log $K_{s0} = -49.7 \pm 0.3$ for reaction (6) at $I = 0.32$ mol dm^{-3} HNO_3. Their data indicate the formation of soluble complexes with phosphoric acid as ligand. Other studies of the speciation of the U(VI)-phosphoric acid system include data suggesting an array of UO_2^{2+}-H_3PO_4-$H_2PO_4^-$-HPO_4^{2-} complexes in the acid pH range (see Table 2). It is important to emphasize that neither H_3PO_4 nor $H_2PO_4^-$ are important complexing agents in most natural water systems. The nature of the complexes formed at higher pH is uncertain. $UO_2(PO_4)_n^{2-3n}$ complexes might be expected in alkaline solutions but have not been reported. Mixed hydroxide-phosphate complexes may also be formed. The determination of the stability constants of these species is difficult due to the possible $CO_2(g)$ contamination in the solubility measurements. Solubility studies are also complicated by the possibility of phase changes of the solid.

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TABLE 1. Some naturally occuring uranyl phosphates

Saleeite	$Mg(UO_2)_2(PO_4)_2 \cdot 8\text{–}10H_2O$
Sabugalite	$HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O$
Metatorbernite	$Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$
Torbernite	$Cu(UO_2)_2(PO_4)_2 \cdot 8\text{–}12H_2O$
Renardite	$Pb(UO_2)_4(PO_4)_2(OH)_4 \cdot 7H_2O$
Dewindtite	$Pb(UO_2)_2(PO_4)_2 \cdot 3H_2O$
Autunite	$Ca(UO_2)_2(PO_4)_2 \cdot 10\text{–}12H_2O$
Uramphite	$NH_4UO_2PO_4 \cdot 3H_2O$
Sodium-Metaautunite	$NaUO_2PO_4 \cdot 3\text{–}4H_2O$
Meta-Autunite. (I and II)	$Ca(UO_2)_2(PO_4)_2 \cdot 0\text{–}6H_2O$
Bassetite	$Fe(UO_2)_2(PO_4)_2 \cdot 8H_2O$
Uranocircite	$Ba(UO_2)_2(PO_4)_2 \cdot 10H_2O$
Meta-Uranocircite	$Ba(UO_2)_2(PO_4)_2 \cdot 6\text{–}8H_2O$
Meta-Ankoleite	$K_{1.7}Ba_{0.2}UO_2PO_4 \cdot 6H_2O$

The objectives of this work are threefold:

1) To study the solubility of the normal uranyl orthophosphate $(UO_2)_3(PO_4)_2 \cdot 4H_2O(s)$ under well-controlled conditions in order to determine the solubility constant of this solid.
2) To establish the composition and stability of the predominant aqueous complexes in the $U(VI)\text{-}H_2O\text{-}H_3PO_4$ system responsible for the solubility of the normal uranyl orthophosphate in the pH range 3 to 9.
3) To discuss the implications of these findings on the mobility of U in natural waters.

EXPERIMENTAL

Reagents

Uranyl nitrate and sodium perchlorate solutions were prepared and analyzed as previously described (BRUNO et al., 1985). All reagents were of analytical grade and all solutions were made with distilled demineralized water from a Millipore Corp. Milli-Q system.

Method

The solid used in these experiments was precipitated from a solution of $UO_2(NO_3)$ by adding a phosphoric acid solution dropwise, under a constant $N_2(g)$ stream, following the method used by VESELY et al. (1965). The temperature was maintained at 25.0 ± 0.5°C. The mixture was agitated during one week. The precipitate which separated after some time was found to be $UO_2HPO_4 \cdot 2H_2O(s)$. (X-ray diffraction pattern JCPDS n°. card 13-61). The uranyl orthophosphate or the normal uranyl phosphate was prepared by repeated digestion of uranyl hydrogen phosphate with water at 80°C. The X-ray diffraction (CuK α radiation) pattern for this solid had sharp peaks, indicating a high degree of crystallinity. The peak positions and intensities were in excellent agreement with the values reported in the literature (JCPDS. 1981).

Three uranyl phosphate samples were dissolved and P and U analysis was performed using ICP. The water content was determined thermogravimetrically. The chemical analysis corresponds to a formula of $(UO_2)_3(PO_4)_2 \cdot 4H_2O(s)$ (see Table 3). The surface area for the starting material (0.9695 m^2/g) was determined by the BET volume method using Kr adsorption. The uranyl orthophosphate was also examined in a JEOL scanning electron microscopy (SEM). The micrographs obtained at a 5000-fold magnification show the needle-like crystals characteristic of the normal uranyl phosphate. The composition and morphology of the solid phase were checked before and after the solubility runs. The analysis indicated no changes in the solid phase during the time of the experiment.

The solubility of this solid has been investigated by potentiometric titrations at 25°C in a 0.5 mol dm^{-3} $NaClO_4$ medium under $N_2(g)$ atmosphere. In order to avoid phase transformations of the solid due to the variation of the phosphate concentration (SCHREYER and BAES, 1954), we worked at a constant total concentration of phosphate and varied the chemical composition of the solution by varying the hydrogen ion concentration. The hydrogen ion concentration was determined using the following cell.

$$-GE/TS/RE+, \qquad (1)$$

where GE stands for the glass electrode. TS for the test solution. and RE for the following reference half cell:

$$NaClO_4/AgClO_4.\ NaClO_4/AgCl.\ Ag. \qquad (2)$$

A typical solubility experiment started with V_0 cm^3 of a 0.5 mol dm^{-3} $NaClO_4$ solution. The initial acidity of the solution H_0 and the E_0 of the glass electrode were determined coulometrically by a Gran titration (GRAN. 1952). A known amount of Na_2HPO_4 was then introduced into the titration vessel in order to achieve the selected total phosphate concentration. 0.01 mol md^{-3}. This phosphate concentration was chosen in order to ensure the stability of the solid phase (SCHREYER and BAES. 1954). At this point a portion of the solid was added to the solution. Its solubility was measured as a function of the acidity of the solution. which was varied coulometrically (BRUNO, 1987). The experimental set-up was connected to a HP-IPC computer and controlled through the AUT program system (ÖSTHOLS. 1988) developed in our department. The attainment of the equilibrium was monitored by measuring the proton concentration. We assumed that equilibrium was obtained when the potential of the glass electrode remained constant within 0.1 mv during 24 h. The results show that the system reached equilibrium in 4 weeks for the first point and in about 10 days for the successive points of the titration.

After equilibrium was attained a sample of the solution was taken for analysis. The solution was immediately filtered through 0.05 or 0.22 μm filters directly into a sample flask. No variations were observed between samples filtered with the two different pore size filters.

TABLE 2. Experimental equilibrium data for the $U(VI)\text{-}H_3PO_4$ system at 25°C, I = 0.* and the corresponding values at 0.5 mol dm^{-3} $NaClO_4$

Equilibrium	$\log \beta^0 \pm 2\sigma$	$\log \beta \pm 2\sigma$
$UO_2^{2+} + H_3PO_4 \rightarrow UO_2H_3PO_4^{2+}$	0.76 ± 0.15	0.80 ± 0.15
$UO_2^{2+} + H_3PO_4 \rightarrow UO_2H_2PO_4^{+} + H^+$	1.12 ± 0.06	0.77 ± 0.07
$UO_2^{2+} + 2H_3PO_4 \rightarrow UO_2(H_3PO_4)(H_2PO_4)^+ + H^+$	1.69 ± 0.15	1.34 ± 0.15
$UO_2^{2+} + 2H_3PO_4 \rightarrow UO_2(H_2PO_4)_2 + 2H^+$	0.87 ± 0.05	0.62 ± 0.06
$H_3PO_4 \rightarrow H_2PO_4^- + H^+$	−2.14 ± 0.03	−1.82 ± 0.04
$H_2PO_4^- \rightarrow HPO_4^{2-} + H^+$	−7.21 ± 0.02	−6.55 ± 0.04
$HPO_4^{2-} \rightarrow PO_4^{3-} + H^+$	−12.35 ± 0.03	−11.32 ± 0.05

* Data selected by the Nuclear Energy Agency (NEA; GRENTHE et al., 1992).

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TABLE 3. Chemical analysis of the solid $(UO_2)_3(PO_4)_2 \cdot 4H_2O(s)$

Content %	Experimental			Theoretical
U	65.6	66.7	67.5	66.6
P	6.0	5.9	5.7	5.8
H_2O	6.5	6.6	7.1	6.7
U/P	10.9	11.3	11.8	11.5

Analysis

Uranium concentrations in solution were determined by a Scintrex UA-3 laser fluorescence analyzer (ROBBINS, 1978). These measurements are based on the fluorescence of a uranyl complex formed by addition of a buffered inorganic complexic agent Fluran. This converts the various uranyl species present in the sample into a single chemical form that has a high luminescence. The detection limit of this analytical technique is $2.1 \cdot 10^{-10}$ mol dm^{-3}. The phosphorus concentration in solution was analyzed using ICP.

Interpretation of the Experimental Data

The solubility reactions used to describe the experimental data can be expressed either by using solubility constants referring to a general equilibria of the type

$$UO_2X_2(s) + qX^- \rightarrow UO_2X_{2+q}^{q-}, \qquad (3)$$

with $K_{s,2+q} = [UO_2X_{2+q}^{q-}]/[X^-]^q$, or by using standard stability constants for complexes,

$$UO_2^{2+} + (q+2)X^- \rightarrow UO_2X_{2+q}^{q-}, \qquad (4)$$

with $\beta_q = [UO_2X_{2+q}^{q-}]/[UO_2^{2+}] \cdot [X^-]^{2+q}$, and the solubility product of the general reaction,

$$UO_2X_2(s) \rightarrow UO_2^{2+} + 2X^-, \qquad (5)$$

with $K_{so} = [UO_2^{2+}] \cdot [X^-]^2$. From Eqs. (3)–(5) it is obvious that $K_{s,2+q} = K_{so} \cdot \beta_q$. The present solubility studies have been made in concentration ranges where the free uranyl concentration $[UO_2^{2+}]$ is very low. Hence, it is not possible to obtain an independent determination of K_{so} and β_q; only constants of the type $K_{s,2+q}$ can be determined.

By combining the solubility data with previous experimental information of the known stability constants of the well-defined complexes, it is possible to obtain a value of K_{so} and the values of the β-constants for other species. This is achieved by writing down a mass balance for the soluble species using the solubility product and β-constants. In the least-squares refinement the equilibrium constants for the known species which are predominant in the experimental ranges investigated are kept constant at the value given by independent methods (cf. Eqn. 4). This method will affect the uncertainty estimates of the equilibrium constants. After fixing the given constants, the uncertainty estimates in the least-squares refinement, $\sigma(\beta)$, refer to the precision of the experiment. In order to estimate the accuracy of the constants, the uncertainty in the calibration constant, $\sigma(K)$, must be considered, giving the overall error equal to $(\sigma^2(\beta) + \sigma^2(K))^{1/2}$.

RESULTS

The solubility data obtained for the three experimental runs are represented in Fig. 1 in the form $\log[U(VI)]_T$ vs. pH (see Table 4). It is helpful to write general reactions describing possible reactants and products for the dissolution of uranyl phosphate in aqueous phosphate solutions. The main reactions involved in this chemical system are

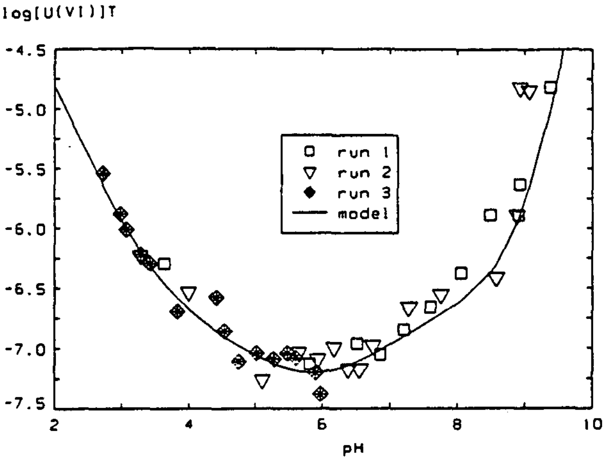

FIG. 1. Solubility curve for the $(UO_2)_3(PO_4)_2 \cdot 4H_2O(s)$ system obtained from the three runs at 0.5 mol dm^{-3} $NaClO_4$, $[PO_4^{3-}]_t = 0.01$ mol dm^{-3} and $T = 25°C$. The theoretical curve has been calculated with the constants given in Tables 2 and 9 at the correspondent ionic strength (0.5 mol dm^{-3} $NaClO_4$).

1) The solubility equilibrium for the uranyl phosphate,

$$(UO_2)_3(PO_4) \cdot 4H_2O(s) \rightarrow 3UO_2^{2+} + 2PO_4^{3-} + 4H_2O, \qquad (6)$$

with $K_{so} = [UO_2^{2-}]^3 \cdot [PO_4^{3-}]^2$;

2) The general hydrolysis equilibria,

$$pUO_2^{2+} + qH_2O \rightarrow (UO_2)_p(OH)_q^{2p-q} + qH^+, \qquad (7)$$

with $\beta_{p,q} = [(UO_2)_p(OH)_q^{2p-q}] \cdot [H^+]^q/[UO_2^{2+}]^p$;

3) The complexation of uranyl by phosphate,

$$aUO_2^{2+} + bH_3PO_4 \rightarrow H_{3b-c}(UO_2)_a(PO_4)_b^{2a-c} + cH^+, \qquad (8)$$

with $K_{a,b} = [H_{3b-c}(UO_2)_a(PO_4)_b^{2a-c}] \cdot [H^+]^c/[UO_2^{2+}]^a \cdot [H_3PO_4]^b$.

A fourth type of reaction would be the formation of mixed hydroxide-phosphate complexes. In aqueous media, it is not possible to distinguish between the following stoichiometries using conventional solution chemical methods:

$$(OH^-)(HPO_4^{2-}) \equiv (PO_4^{3-})(H_2O)$$

and

$$(OH^-)(H_2PO_4^-) \equiv (HPO_4^{2-})(H_2O).$$

This problem is also encountered when studying hydroxide and carbonate complexes (BRUNO et al., 1987; GRENTHE and LAGERMAN, 1991).

The analysis of the data will be performed stepwise. In a first stage we will discuss the possible U(VI)-hydroxide complexes formed in the pH range of interest. Afterwards, we will consider the entire $U(VI)-H_2O-H_3PO_4$ system.

TABLE 4. Experimental data for the system U(VI)-H_3PO_4-H_2O at 0.5 mol dm^{-3} $NaClO_4$, $[PO_4^{3-}]_T$ = 0.01 mol dm^{-3} and 25°C

	pH	$[U(VI)]_T$
Run No. 1	3.635	5.047e-07
	5.820	7.464e-08
	6.517	1.091e-07
	6.851	8.831e-08
	7.212	1.429e-07
	7.603	2.193e-07
	8.059	4.197e-07
	8.497	1.294e-06
	8.910	1.285e-06
	8.927	2.317e-06
	9.379	1.510e-05
Run No. 2	3.286	5.875e-07
	3.994	2.897e-07
	5.109	5.457e-08
	5.659	9.247e-08
	5.934	8.147e-08
	6.178	1.009e-07
	6.390	6.714e-08
	6.557	6.730e-08
	6.744	1.049e-07
	7.282	2.188e-07
	7.758	2.773e-07
	8.583	3.819e-07
	8.887	1.274e-06
	8.939	1.503e-05
	9.072	1.416e-05
Run No. 3	2.718	2.884e-06
	2.988	1.312e-06
	3.073	9.727e-07
	3.292	5.984e-07
	3.428	5.058e-07
	3.837	2.018e-07
	4.408	2.630e-07
	4.533	1.387e-07
	4.748	7.762e-08
	5.019	9.120e-08
	5.273	8.128e-08
	5.473	9.120e-08
	5.603	8.318e-08
	5.909	6.309e-08
	5.980	4.169e-06

U(VI)-H_2O System

The stoichiometry and stability of the hydroxide complexes of the uranyl ion, UO_2^{2+}, have been discussed by a large number of authors (BAES and MESMER, 1976; SYLVA and DAVIDSON, 1979; MUSIKAS, 1972; GRENTHE et al., 1992). Most of the studies were done under acidic conditions, where cationic species are responsible for the solubility of U(VI).

The study of species in neutral and alkaline solutions of U(VI) is complicated by the formation of a number of sparingly soluble solid phases and by the possible $CO_2(g)$ contamination which produces strong carbonate complexes such as $UO_2(CO_3)^{2-}$, $UO_2(CO_3)_3^{4-}$, and $(UO_2)_3(CO_3)_6^{6-}$ (GRENTHE et al., 1984; GRENTHE and LAGERMAN, 1991). There is experimental evidence for the existence of anionic U(VI) hydrolysis species. Several complexes have been proposed, mainly $(UO_2)_3(OH)_7^-$ (SUTTON, 1947; TSYMBAL, 1969; TRIPATHI, 1983), $UO_2(OH)_3^-$ (BRUNO and SANDINO, 1989), and $UO_2(OH)_4^{2-}$ (MUSIKAS, 1972). GRENTHE et al. (1992) have done a comprehensive review of the hydrolysis of U. Their selected constants are listed in Table 5 together with the ones previously reported by the authors.

Schoepite $UO_2(OH)_2 \cdot H_2O(s)$ (chemically equivalent to $UO_3 \cdot 2H_2O(s)$) is the stable U(VI) hydroxide at low temperatures (HOSTETLER and GARRELS, 1962). Although not frequently, it has been identified in some geological environments (FINCH and EWING, 1992) and has also been found as a weathering product of uraninite under oxidizing conditions (WANG, 1981). This phase has also been identified as a corrosion product of spent fuel in long-term leaching experiments under oxidizing conditions, (WANG and KATAYAMA, 1982; STROES-GASCOYNE et al., 1985).

In a previous study (BRUNO and SANDINO, *1989*), we investigated the solubility of schoepite in neutral and alkaline media by potentiometric titrations at 25°C in 0.5 mol dm^{-3} $NaClO_4$ solution. The experimental data are given in Table 6. Two phases with different degrees of crystallinity were studied. The data indicated the predominance of the species $(UO_2)_3(OH)_5^+$, $(UO_2)_3(OH)_7^-$, and $UO_2(OH)_3^-$. We have further analyzed these experimental data, and we can confirm the chemical model but with slightly different values for the equilibrium constants.

The potentiometric data have been treated using the computer program C-LETAGROP (ÖSTHOLS, 1991). The calculations were carried out on a CONVEX 210 computer. This program varies the equilibrium constants of the chemical system tested so as to minimize the sum of squares of the differences between the calculated and measured solubilities. It can also treat systematic errors and make error estimates of the fitted parameters based on the errors in the experimental measured quantities using the MonteCarlo method. It can treat data of the form $(-\log [H^+], [U(VI)]_T)_i$, where i = 1, 2, 3, etc., and represent the separate experimental runs, and $[U(VI)]_T$, the total concentration of dissolved U(VI).

The experimental data $(-\log [H^+], [U(VI)]_T)_i$ for each run i (amorphous and crystalline phases) were first treated separately. The corresponding solubility constant K_{so}, for the reaction

TABLE 5. Selected formation constants for the U(VI)-H_2O system at 25°C, I = 0 and the corresponding values at 0.5 mol dm^{-3} $NaClO_4$

$$pUO_2^{2+} + qH_2O \rightarrow (UO_2)_q(OH)_q^{2p-q} + qH^+$$

(p, q)	$\log \beta^0_{p,q} \pm 2\sigma$	$\log \beta_{p,q} \pm 2\sigma$	Source
(1, 1)	−5.20 ± 0.30	−5.54 ± 0.30	(a)
(1, 2)	<−10.3		(a)
(2, 2)	−5.62 ± 0.04	−5.92 ± 0.04	(a)
(3, 4)	−11.9 ± 0.3	−12.6 ± 0.3	(a)
(3, 5)	−15.55 ± 0.12	−16.54 ± 0.14	(a)
(4, 7)	−21.9 ± 1.0	−23.0 ± 1.0	(a)
(1, 3)	−19.13 ± 0.4	−19.2 ± 0.4	(a)
	−19.69 ± 0.01	−20.2 ± 0.1	(b)
(3, 7)	−31.5 ± 2.0	−31.0 ± 2.0	(a)
	−31.9 ± 0.1	−31.4 ± 0.1	(b)

Data from (a) GRENTHE et al. (1992)
(b) BRUNO and SANDINO (1989)

TABLE 6. Experimental data for the Schoepite solubility system, $UO_2(OH)_2 \cdot H_2O$, at 0.5 mol dm^{-3} $NaClO_4$ and 25°C

	pH	$[U(VI)]_T$
Amorphous	6.873	8.128e-04
	7.001	4.786e-04
	7.201	3.890e-04
	7.299	2.188e-04
	7.430	1.380e-04
	7.512	1.230e-04
	7.621	1.380e-04
	7.770	1.122e-04
	7.779	1.445e-04
	7.821	1.380e-04
	7.902	1.349e-04
	7.938	2.455e-04
	8.031	2.828e-04
	8.149	4.169e-04
Crystalline	6.830	6.310e-05
	6.857	5.623e-05
	6.959	5.129e-05
	7.124	2.884e-05
	7.212	2.630e-05
	7.383	1.862e-05
	7.489	1.479e-05
	7.612	1.349e-05
	7.703	1.148e-05
	7.853	6.761e-06
	7.875	8.318e-06
	7.880	7.586e-06
	7.901	7.413e-06
	8.094	5.248e-06
	8.233	4.898e-06
	8.284	4.467e-06
	8.313	9.120e-06
	8.341	4.074e-06
	8.821	3.020e-05

$$UO_2(OH)_2 \cdot H_2O(s) + 2H^+ \rightarrow UO_2^{2+} + 3H_2O, \quad (9)$$

along with the β-values for the general hydrolysis equilibria (7), were calculated using the stability constants for the hydrolysis of U(VI) recommended by NEA (GRENTHE et al., 1992). From the values listed in Table 5, it is clear that the neutral species $UO_2(OH)_2(aq)$ is not as well defined as the polynuclear species $(UO_2)_4(OH)_7^+$. In order to calculate the values for the aqueous species $UO_2(OH)_3^-$ and $(UO_2)_3(OH)_7^-$ along with the corresponding solubility products with a better accuracy (see Interpretation of the Experimental Data section), these two species were not included in the chemical model. The results of these calculations are given in Table 7. The agreement between the experimental and theoretical data calculated with these models is shown in Fig. 2a and b in the form $[U(VI)]_T$ vs. pH. As seen from these figures, the model is better defined in the case of the crystalline phase (see Fig. 2b) than in the amorphous one. From Fig. 2a it is clear that the fit between chemical model and experimental data is fair, except around the solubility minimum. The fact that the experimental solubilities are lower than the calculated ones could be explained in terms of phase stability, i.e., the amorphous phase is gradually transformed to a more crystalline solid. The solubility of these two solid phases is explained with the same chemical model (major species $(UO_2)_3(OH)_5^+$, $(UO_2)_3(OH)_7^-$, and $UO_2(OH)_3^-$). The calculated equilibrium constants of the two anionic complexes (see Table 7) for the two sets of data are slightly different. These discrepancies could be due to the omission of some other relevant complexes. Further calculations, including the species $UO_2(OH)_2(aq)$ and $(UO_2)_4(OH)_7^+$, did not improve the model. We also made an attempt to treat jointly the two sets of data. In this way, a common value for the corresponding aqueous species was obtained. Nevertheless, the least-square refinement yields a higher minimum, indicating that the fit was not as good as the previous fit calculated. Hence, the equilibrium constants given in Table 7 correspond to the best chemical model obtained.

The hydrolysis system of U(VI) under the experimental conditions of our study is quite difficult to resolve since several species are coexisting. Therefore, the values for the equilibrium constants are strongly correlated with each other. To a certain extent, these difficulties are still reflected in the hydrolysis constant values obtained for the two anionic complexes, $UO_2(OH)_3^-$ and $(UO_2)_3(OH)_7^-$, given in Table 7. Numerically, one could say that the polynuclear species is better defined in the amorphous data set than in the crystalline one, whereas the $UO_2(OH)_3^-$ species is more accurately defined in the crystalline case. This is clearly correlated to the corresponding total U concentration of the two sets of data. Certainly, a better model of the UO_2^{2+} hydrolysis in the neutral to alkaline pH range could be obtained by a combination of potentiometric and spectroscopic studies. The solubilities of the two schoepite forms, here reported, provide a good confirmation of the amphoteric behaviour of U(VI) in aqueous solutions despite the evident discrepancies obtained in the numerical model, which could be also due to the existence of unrecognized systematic errors. The corresponding mean values for the hydrolysis constants of the species $UO_2(OH)_3^-$ and $(UO_2)_3(OH)_7^-$ are also listed in Table 7.

TABLE 7. Set of equilibrium constants obtained from solubility data of Schoepite, $UO_2(OH)_2 \cdot H_2O(s)$, at 0.5 mol dm^{-3} $NaClO_4$ and 25°C

	log β ± 2σ	
Equilibrium	Amorphous	Crystalline
$3UO_2^{2+} + 7H_2O \rightarrow (UO_2)_3(OH)_7^- + 7H^+$	−32.00 ± 0.17	−33.32 ± 0.22
	Mean value*	−32.7 ± 0.8
$UO_2^{2+} + 3H_2O \rightarrow UO_2(OH)_3^- + 3H^+$	−19.83 ± 0.34	−20.18 ± 0.19
	Mean value*	−20.0 ± 0.5
	log K_{s0} ± 2σ	
$UO_2(OH)_2 \cdot H_2O + 2H^+ \rightarrow UO_2^{2+} + 3H_2O$	6.59 ± 0.14	6.23 ± 0.14

* The uncertainty assigned to the mean value (m) is calculated using the following equation, $\sigma = |x_i - m| + \sigma_{max}$, where x_i corresponds to one of the constant values and σ_{max} is the larger one of the two uncertainties σ_i.

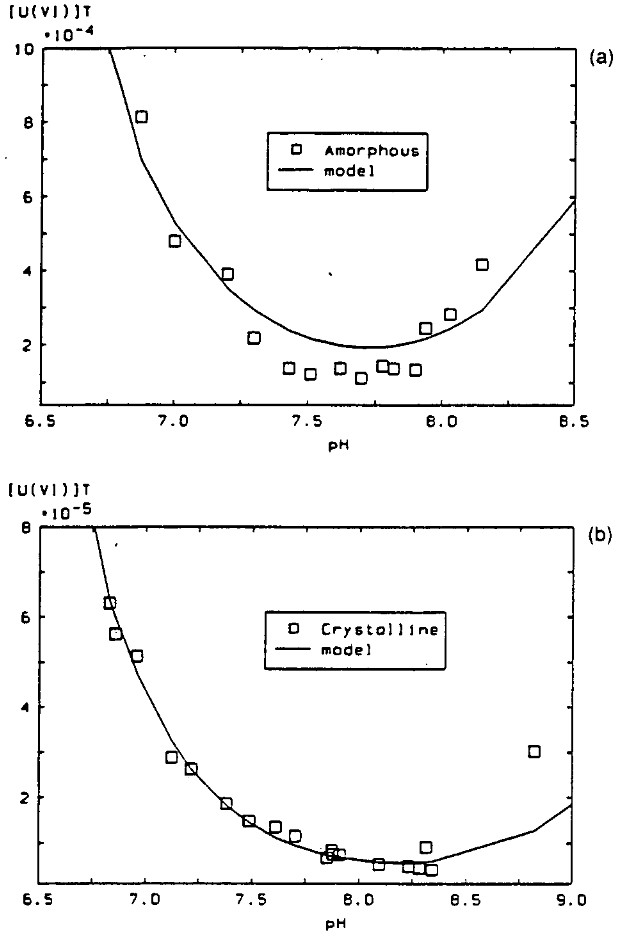

FIG. 2. Solubility curves of the experimental data in the schoepite system obtained at 0.5 mol dm^{-3} $NaClO_4$ and T = 25°C. (a) Amorphous phase. (b) Crystalline phase. The theoretical curves have been calculated using the constants listed in Tables 5 and 7.

The equilibrium constant for the complex $(UO_2)_3 \times (OH)_7^-$ reported in this study, as well as the preliminary proposed values by the authors (BRUNO and SANDINO, 1989), results in a considerable improvement of the agreement between calculated and experimental U solubilities at alkaline pH values (BRUNO and PUIGDOMENECH, 1989). In a previous investigation (BRUNO and SANDINO, 1989), we pointed out that the previous reported value of the stability constant $\beta_{3,7}$ (SUTTON, 1947; TSYMBAL, 1969) was overestimated, being the proposed value of the order of log $\beta_{3,7} = -28$.

At the lower total solution concentrations of U (the case of the crystalline schoepite), the mononuclear species $UO_2(OH)_3^-$ predominates over the polynuclear complexes. However, the present solubility study of the uranyl orthophosphate phase (see the following section) allows us a more precise determination of this constant since the total U concentration is very low and the polynuclear complexes are present in very small amounts. In the phosphate system the complex $UO_2(OH)_3^-$ is present as a predominant species at the highest pH values (see Fig. 3). The value of log $\beta_{1,3} = -19.67 \pm 0.17$ is in fair agreement with the mean value estimated from the schoepite study, log $\beta_{1,3} = -20.0 \pm 0.5$ (see Interpretation of the Experimental Data section for a discussion of the precision and the accuracy of the constants).

Finally, a modified version (PUIGDOMENECH, 1983) of the SOLGASWATER program has been used to compute the distribution for U under these experimental conditions. The relative distribution of the proposed species is shown in Fig. 4a and b. From these diagrams it is clear that the predominant species at the lowest pH is the well-established $(UO_2)_3(OH)_5^+$ complex, whereas at the highest pH the major species are the anionic complexes $UO_2(OH)_3^-$ and $(UO_2)_3(OH)_7^-$, depending on the total U concentration in solution. It should be noticed that the range of predominance of these species is not very much affected by the differences in the corresponding equilibrium constants.

The equilibrium constants have been extrapolated to the infinite dilution state by using SIT, the specific ion interaction theory (GRENTHE and WANNER, 1989). In this approach the activity coefficient (δ) of a certain species i is given by

$$\log \delta_i = -z_i^2 \cdot D + \sum_j \epsilon(i,j) \cdot m_j, \tag{10}$$

where z_i is the charge of the ion i, $\Sigma_j \epsilon(i,j)$ is the summation of the interaction coefficient (ϵ) of the ion i with all ions j of opposite charge, D is the Debye-Hückel term, $D = 0.5109 \cdot \sqrt{I}/(1 + 1.5 \cdot \sqrt{I})$, and m_j is the molality of the ionic medium. The interaction coefficients used in these calculations are $\epsilon(UO_2^{2+}, ClO_4^-) = 0.46 \pm 0.03$, $\epsilon((UO_2)_3 \times OH)_7^-, Na^+) \equiv \epsilon(UO_2(OH)_3^-, Na^+) = -0.09 \pm 0.05$, $\epsilon(UO_2)_3(OH)_5^+, ClO_4^-) = 0.51 \pm 0.15$, $\epsilon(H^+, ClO_4^-) = 0.14 \pm 0.02$ (GRENTHE and WANNER, 1989). The results are shown in Table 8.

U(VI)-H_2O-H_3PO_4 System

The first step in the interpretation of our solubility data was to assume only the formation of hydroxide complexes. Clearly, the high U concentrations are not only due to the

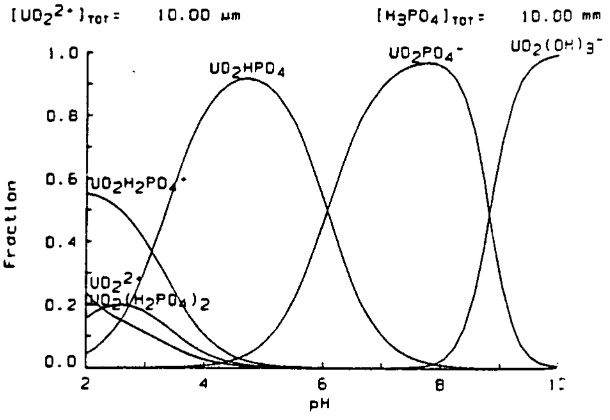

FIG. 3. Distribution diagram for the aqueous species in the system U(VI)-H_3PO_4-H_2O as calculated from the constants given in Tables 2 and 9, at I = 0.5 mol dm^{-3} $NaClO_4$ and T = 25°C.

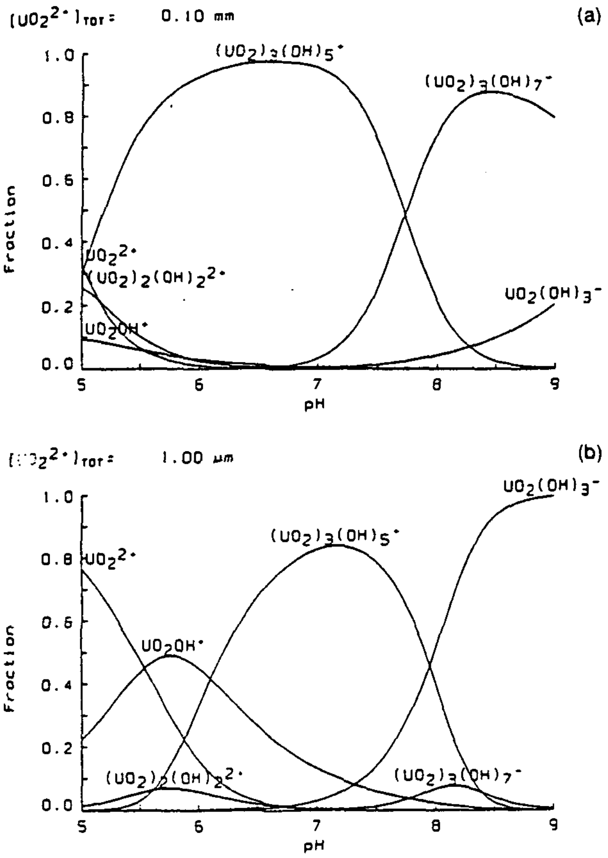

FIG. 4. Distribution diagrams for the aqueous species in the U(VI)-H_2O system as calculated from the constants given in Tables 5 and 7. (a) Amorphous schoepite. (b) Crystalline schoepite.

formation of these species but rather to one or more complexes involving phosphate ligands. The dependence of log$[U(VI)]_T$ on pH (see Fig. 1) shows four different zones:

1) In the pH range 2 to 5 the data can be approximated to a straight line of slope −0.5. This indicates the coexistence of one positively charged complex and one neutral species (JOHANSSON, 1968). From the previous studies (see Table 2) we can deduce that $UO_2H_2PO_4^+$ is the positively charged complex. The neutral complex should have the general composition $H_{3b-c}(UO_2)_a(PO_4)_b^{2a-c}$. If only mononuclear complexes are assumed, $a = 1$ and $c = 2$. Hence, the neutral complex should have the general stoichiometry $H_{3b-2}UO_2(PO_4)_b$.
2) In the pH range 5.5 to 6.5 there is no dependence of the solubility with pH. Hence, the predominant species is uncharged.
3) In the pH range 6.5 to 8.0 the solubility data can be approximated to a straight line of slope +0.5. This indicates that a negatively charged (−1) complex is formed, in addition to the neutral one. Again, if we assume the formation of mononuclear complexes, $a = 1$ and $c = 3$, the stoichiometry for this complex would be $H_{3b-3}UO_2(PO_4)^-$.
4) Finally, at pH > 8.5 the dependence of log $[U(VI)]_T$ on pH can be approximated to a straight line of slope +1, indicating the predominance of the complex $H_{3b-3}UO_2(PO_4)_b^-$.

The value of b was determined by comparing systematically the experimental and theoretical solubilities calculated using a modified version of HALTAFALL computer program (INGRI et al., 1967). The best agreement was obtained for $b = 1$. Hence, the proposed species are $UO_2HPO_4(aq)$ and $UO_2PO_4^-$. In addition, the known $UO_2(OH)_3^-$ hydroxide complex proved to be dominant in the most alkaline pH range.

The stability constants of these three species were calculated as well as the corresponding solubility constant. The potentiometric data of the three experimental runs were treated using the computer program C-LETAGROP (ÖSTHOLS, 1991), considering all the phosphate complexes listed in Table 2 along with the hydrolysis species previously selected. The equilibrium constants of the best model are given in Table 9 at 0.5 mol dm^{-3} $NaClO_4$ and 25°C. The agreement between the experimental and theoretical data calculated with the given model is shown in Fig. 1. The relative distribution of the species proposed in this study, under the conditions of the measurements, is shown in Fig. 4.

These equilibrium constants have been extrapolated to the infinite dilution standard state by using the SIT theory (GRENTHE and WANNER, 1989). The interaction coefficients used in these calculations are $\epsilon(UO_2^{2+}, ClO_4^-) = 0.46 \pm 0.03$, $\epsilon(HPO_4^{2-}, Na^+) = -0.15 \pm 0.06$, $\epsilon(PO_4^{3-}, Na^+) = -0.25 \pm 0.03$, $\epsilon(UO_2PO_4^-, Na^+) = \epsilon(UO_2(OH)_3^-, Na^+) = -0.09 \pm 0.05$ (GRENTHE and WANNER, 1989). The results are also shown in Table 9.

There are some previous determinations of the solubility product of similar solid phases. Comparison of the results of this study with the findings of other researchers may seem straightforward, but for a number of reasons this is not so. In order to calculate thermodynamic values from solubility

TABLE 8. Set of equilibrium constants obtained from solubility data of Schoepite, $UO_2(OH)_2 \cdot H_2O(s)$, extrapolated to the infinite dilution standard state

	log $\beta^0 \pm 2\sigma$	
Equilibrium	Amorphous	Crystalline
$3UO_2^{2+} + 7H_2O \rightarrow (UO_2)_3(OH)_7^- + 7H^+$	−31.55 ± 0.17	−32.87 ± 0.22
	Mean value*	−32.2 ± 0.8
$UO_2^{2+} + 3H_2O \rightarrow UO_2(OH)_3^- + 3H^+$	−19.90 ± 0.34	−20.25 ± 0.19
	Mean value*	−20.1 ± 0.5
	log $K_{s0}^0 \pm 2\sigma$	
$UO_2(OH)_2 \cdot H_2O + 2H^+ \rightarrow UO_2^{2+} + 3H_2O$	6.33 ± 0.14	5.97 ± 0.14

* See Table 7.

TABLE 9. Set of equilibrium constants obtained from solubility data of $(UO_2)_3(PO_4)_2\cdot 4H_2O(s)$ at 0.5 mol dm^{-3} $NaClO_4$ and T = 25°C. and the extrapolated values to the infinite dilution standard state

Equilibrium	log $\beta \pm 2\sigma$	log $\beta^0 \pm 2\sigma$
$UO_2^{2+} + HPO_4^{2-} \rightarrow UO_2HPO_4$	6.03 ± 0.09	7.28 ± 0.10
$UO_2^{2+} + PO_4^{3-} \rightarrow UO_2PO_4^-$	11.29 ± 0.08	13.25 ± 0.09
$UO_2^{2+} + 3H_2O \rightarrow UO_2(OH)_3^- + 3H^+$	−19.67 ± 0.17	−19.74 ± 0.18
$(UO_2)_3(PO_4)_2\cdot 4H_2O(s) \rightarrow 3UO_2^{2+} + 2PO_4^{3-} + 4H_2O$		
$\log K_{so} \pm 2\sigma = -48.48 \pm 0.16$	$\log K^0_{so} \pm 2\sigma = -53.32 \pm 0.17$	

data, it is first necessary to determine the stoichiometries of the dominant aqueous species, as the solubility constant depends on the chemical model and the numerical values of the various complex formation constants. This was not always done in previous studies. Another important factor to consider is the influence of the ionic strength on the equilibrium constants of these complexes. We have recalculated the literature values to the zero ionic strength standard state by using SIT. the specific ion interaction theory (Grenthe and Wanner. 1989).

Karpov (1961) studied the solubility of the phase $(UO_2)_3(PO_4)\cdot 6H_2O(s)$ in nitric acid solutions and determined the solubility product to be $\log K_{so} = -46.3$, whereas the corrected value and extrapolated to $I = 0$ is $\log K^0_{so} = -48.7$. The increase of solubility in comparison to the tetrahydrated form is expected from a more hydrated solid phase. Vesely et al. (1965) studied the solubility of $(UO_2)_3(PO_4)_2\cdot 4H_2O(s)$. The solubility data that they reported have been recalculated using the procedures for activity coefficients corrections recommended by NEA (Grenthe and Wanner, 1989) and the selected stability constants for the U(VI)-phosphate complexes (see Table 2) formed in the pH range of the study; pH: 0.5–3. The solubility constant extrapolated to the infinite dilution standard state using SIT is $\log K^0_{so} = -49.4 \pm 0.3$. This value corresponds clearly to a more soluble phase. Vesely et al. (1965) did not report any X-ray diffraction investigation or specific surface area measurement of the phase they used. The higher solubility may be a result of the use of a less crystalline phase in that work. In the present investigation, we have calculated the solubility product using data from a pH range where the free uranyl concentration $[UO_2^{2+}]$ accounts at most for 20% of the total dissolved U (see Fig. 4). This will make the determination of the solubility constant rather uncertain. Hence, following the procedure described before, we have determined the solubility constant K_{so} for the reaction (6) on the basis of the well-known stability constants for the phosphate complexes previously reported, i.e., by combining the equilibrium constant for the reaction

$$\tfrac{1}{3}(UO_2)_3(PO_4)_2\cdot 4H_2O(s) + \tfrac{1}{3}H_3PO_4 + H^+ \rightarrow UO_2H_2PO_4^+ + \tfrac{4}{3}H_2O \quad (11)$$

with the stability constant for the formation of the complex $UO_2H_2PO_4^+$, since this species is the predominant one at the lowest pH of the present study and has been previously rather well determined. In a recent publication on the complexation of the uranyl ion with phosphate (Mathur, 1991), a value for the stability constant of this species has also been given. In our calculations we have used the numerical value selected and recommended by NEA (see Table 2) for the following reaction:

$$UO_2^{2+} + H_3PO_4 \rightarrow UO_2H_2PO_4^+ + H^+. \quad (12)$$

In this study we have established the existence of two U(VI)-phosphate complexes, $UO_2HPO_4(aq)$ and $UO_2PO_4^-$, and determined their stability constants. The existence of the neutral species $UO_2HPO_4(aq)$ has been previously proposed by Moskvin et al. (1967). They studied the solubility of $UO_2HPO_4\cdot 4H_2O(s)$ in different ionic media under very acidic conditions. However, their interpretation of the data was based on the formation of only two phosphate species, $UO_2HPO_4(aq)$ and $UO_2(HPO_4)_2^{2-}$, ignoring the complex formation between UO_2^{2+} and $H_3PO_4/H_2PO_4^-$. Hence, their stability constants were bound to be highly overestimated. Dongarra and Langmuir (1980) performed a potentiometric study of the U(VI) phosphate system at quite low pH (pH < 4.9). They also reported stability constants for the formation of the anionic complex $UO_2(HPO_4)_2^{2-}$ based on the values proposed by Moskvin et al. (1967).

The shortcomings of these two studies have been thoroughly discussed and criticized by different authors (Tripathi, 1983; Grenthe et al., 1992). Their analysis of the data indicated that the proposed chemical model was incompatible with the given stability constant values, especially in the case of the species $UO_2(HPO_4)_2^{2-}$. The formation of this complex is not compatible with the dependence of the total U concentration with pH and phosphate concentration that we observe in our solubility measurements. This is illustrated in Fig. 5 where the theoretical model was obtained considering the existence of this species along with the speciation model proposed by Langmuir (1978). The figure indicates that by using the model proposed by the authors the solid $(UO_2)_3(PO_4)_2\cdot 4H_2O(s)$ is not stable under the experimental conditions of our investigation. Further calculations using the PHREEQE code (Parkhurst et al., 1980) in combination with the thermodynamic data base proposed by Langmuir (1978) indicated that the formation of this solid phase at $[PO_4^{3-}]_T = 0.01$ mol dm^{-3} requires a total U concentration higher than 0.001 mol dm^{-3}. As we mentioned before, Tripathi (1983) performed a careful analysis of this chemical system. His calculations also show that all the solutions in the work of Dongarra and Langmuir (1980) were supersaturated with respect to the uranyl orthophosphate solid phase.

Our solubility data indicated the formation of other anionic complex, $UO_2PO_4^-$, which is responsible for the increase of solubility of $(UO_2)_3(PO_4)_2\cdot 4H_2O(s)$ in the pH range [illegible] to 8. It might appear somehow surprising that the phosphate ligand is already deprotonated at this pH range. However, it is well known that the acidity of protonated ligands is strongly increased on coordination to metal ions, and the interpretation of our solubility data clearly indicates the formation

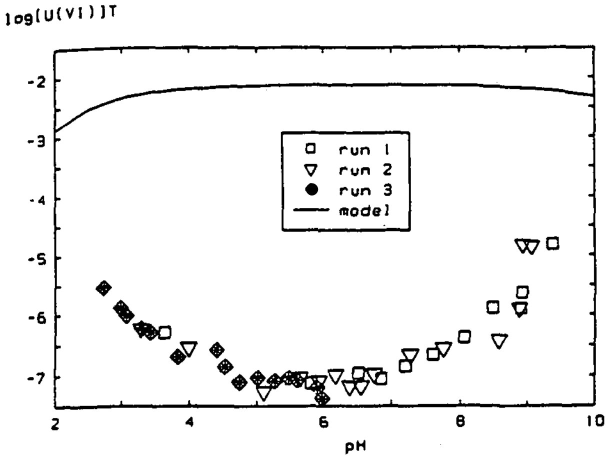

FIG. 5. Solubility curve calculated with LANGMUIR (1978) thermodynamic data base including the species $UO_2(HPO_4)_2^{2-}$, compared with experimental values as a function of pH at 25°C and $I = 0.5$ mol dm^{-3}.

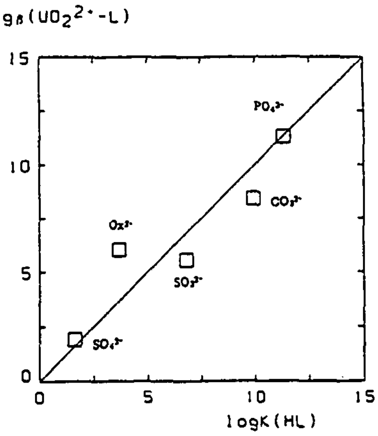

FIG. 6. Log $\beta(UO_2^{2+}\text{-L})$ as a function of log K(HL) for the complexes listed in Table 10.

of this complex. We have previously addressed the strong tendency of U(VI) to form complexes with O-containing ligands. Some of these complexes (carbonate, sulfate, oxalate (Ox^{2-}), and sulfite are well-established examples) have an additional common feature: they involve bidentate coordination of oxygen donors in the ligand. In the case of phosphate the same kind of bonding might be expected. One possibility to test this proposal is to use linear free energy (LFE) relationships (ROSSOTTI, 1960). LFE relationships have been used in many areas of chemistry to correlate properties of various types. In coordination chemistry it is common to correlate the Bronsted basicity of the ligand with its Lewis basicity as measured by the complex formation constants to various donors. Correlation with the stability of the complex (ML) with the acidity constant of the ligand (HL) has shown that linear plots are only obtained for series of ligands which are structurally related. Fig. 6 shows such a LFE relationship for UO_2^{2+} complexes with the ligands SO_4^{2-}, Ox^{2-}, SO_3^{2-}, CO_3^{2-}, and PO_4^{3-}. The thermodynamic data used in this diagram are listed in Table 10. This plot clearly indicates a cor relation between the strength of the conjugate bases (HL^{n-}) and the stability of the complexes (UO_2L^{2-n}). This is an indication that all ligands might be bonded in the same way, which gives additional support to the formation and stability of $UO_2PO_4^-$.

The steep increase in the solubility of $(UO_2)_3(PO_4)_2 \times 4H_2O(s)$ in the pH range 8 to 9 is due to the formation of $UO_2(OH)_3^-$ in addition to the $UO_2PO_4^-$ species. As we have already discussed, we have been able to establish the formation constant of this species in a more precise way in the present study (see Table 9).

The question that remains to be answered is what is the relative importance of phosphate complexation in the aqueous speciation of U(VI) in groundwaters. In Fig. 7 we show a calculated predominance diagram for aqueous U(VI) under conditions that cover a wide range of natural aqueous systems, assuming that the total carbonate concentration is $10^{-3.5}$ mol dm^{-3}, the world average for natural waters (STUMM and MORGAN, 1981). The diagram clearly shows that phosphate complexation can dominate over the strong carbonate species under certain conditions. Considering that the $[CO_3^{2-}]_T/[H_3PO_4]_T$ concentration ratio in natural aqueous systems is highly variable, our results point out the relative importance of the phosphate complexation. The same pattern has been recently found in the case of rare earth elements. BYRNE et al. (1991) showed that the phosphate complexation is a predominant process when the ratio $[HPO_4^{2-}]/[HCO_3^-]$ is greater than $1 \cdot 10^{-3}$, which indicates the potential importance of the phosphate ligand in natural waters. Therefore, there is a clear need of considering the uranyl phosphate species in the geochemical modelling of U. Previous works on this subject were bound to overestimate the formation of the U(VI)-phosphate complexes, since most of the current data bases appear to be based on quite erroneous thermodynamic data (e.g., the species $UO_2(HPO_4)_2^{2-}$ previously commented).

TABLE 10. Equilibrium constants for the UO_2^{2+}-L and HL systems at 25°C and I = 0.5 mol dm^{-3} $NaClO_4$

Equilibrium	log β	Source
$UO_2^{2+} + CO_3^{2-} \rightarrow UO_2CO_3$	8.44	(a)
$UO_2^{2+} + SO_4^{2-} \rightarrow UO_2SO_4$	1.92	(a)
$UO_2^{2+} + SO_3^{2-} \rightarrow UO_2SO_3$	5.54	(a)
$UO_2^{2+} + Ox^{2-} \rightarrow UO_2Ox$	6.02	(b)
$UO_2^{2+} + PO_4^{3-} \rightarrow UO_2PO_4^-$	11.28	(c)
$HCO_3^- \rightarrow CO_3^{2-} + H^+$	−9.92	(a)
$HSO_4^- \rightarrow SO_4^{2-} + H^+$	−1.62	(a)
$HSO_3^- \rightarrow SO_3^{2-} + H^+$	−6.83	(a)
$HOO_4^{2-} \rightarrow PO_4^{3-} + H^+$	−11.32	(a)
$HOx- \rightarrow O^{2-} + H^+$	−3.67	(b)

(a) Data from GRENTHE et al. (1992)
(b) Data from PERRIN (1979)
(c) Data from this work

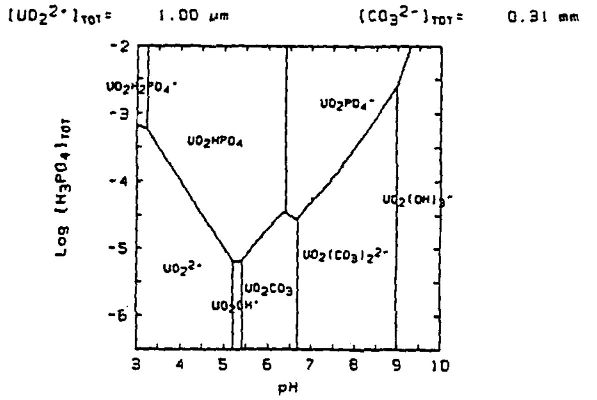

FIG. 7. Predominance-area diagram for the system U(VI)-CO_2-H_3PO_4-H_2O in aqueous phase at 25°C.

CONCLUSIONS

The experimental determination of the solubility of the uranyl orthophosphate $(UO_2)_3(PO_4)_2 \cdot 4H_2O(s)$ has been carried out at 25°C and $I = 0.5$ mol dm^{-3} $NaClO_4$. Under these conditions the calculated solubility product for reaction (6) is log $K_{s0} = -48.48 \pm 0.16$, whereas the extrapolated value to the standard state is log $K^0_{s0} = -53.32 \pm 0.17$.

The experimental data can be described in terms of the following predominant species: the phosphate complexes $UO_2H_2PO_4^+$, $UO_2HPO_4(aq)$, $UO_2PO_4^-$, together with the hydrolysis species $UO_2(OH)_3^-$. By using recent literature values for the equilibrium constants of the hydrolysis species we have recalculated the stability of $(UO_2)_3(OH)_7^-$ and $UO_2(OH)_3^-$ complexes, and the solubility product of schoepite $(UO_2(OH)_2 \cdot H_2O(s))$ as well. The stability of the complexes $UO_2H_2PO_4^+$ and $(UO_2)_3(OH)_7^-$ has been confirmed.

While an attempt has been made in these investigations to determine the solubility constants of these solid phases as well as the formation constants of those complexes, it must be pointed out that these numerical values have an inherent uncertainty due to the low free-uranyl concentration found under these experimental conditions.

A comparison of the relative stability of phosphate, hydroxide, and carbonate complexes indicates that the uranyl phosphate complexation dominates over a range of chemical conditions, especially at neutral pH, even if the existence of the very strong uranyl carbonate complexes is considered. This confirms the correlation found in some granitic groundwaters between the U and phosphate concentrations.

Speciation models are generally constructed by compiling available thermodynamic data. One important problem is the neglect of significant ligands. Another important problem follows from the lack of appropriate of equilibrium data together with the poor quality of some of these thermodynamic data. In view of the present results, the use of $UO_2(HPO_4)_2^{2-}$ should be totally discarded in the geochemical modelling of U in natural systems.

The geochemistry of U dissolution, transport, and precipitation by and from aqueous solutions are subjects of intense research. The results of this study can be combined with previous works on geochemical modelling of U to better understand the processes which control the migration of this element in natural environments.

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