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Advances in investigation of dioxouranium(VI) complexes of interest for natural fluids.

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Abstract

The interactions of dioxouranium(VI) cation with different organic and inorganic ligands of environmental and biological interest were carefully examined with the aim to draw a chemical speciation picture of this ion in natural aquatic ecosystems and in biological fluids. Since UO_2^{2+} ion shows a significant tendency to hydrolyze, particular attention was paid in considering the hydrolysis species formation both in the presence and in absence of ligands. The results reported in the literature show that formation of the hydrolytic species assumes a great importance in the complexation models for all the UO_2^{2+} -ligand systems considered. In particular, the following ligands have been taken into account: i) hydroxyl, chloride, fluoride, sulfate, carbonate and phosphate, as inorganic ligands, and ii) carboxylates (with particular reference to oxalate and citrate), amines, amino acids, poly(amino carboxylates) (complexones), nucleotides, phosphonates, mercapto compounds and sulfonates, as organic ligands. In order to elucidate the speciation of uranyl in the presence of dissolved natural organic matter, the interactions with humic and fulvic acids were also considered. The strength of interaction in all the systems considered was expressed in terms of stability constants of complex species and, if available, of the relative thermodynamic stability parameters. When possible, if data reported in the literature were sufficiently homogeneous, trends of stability were found for the different ligands of the same class and for ligands of different classes. Moreover, relationships were derived for poly-functional ligands, such as poly-carboxylate, poly-amine and poly(amino carboxylate) ones, useful to predict the stability constants as a function of the number of binding sites per molecule, considering also, as in the case of amino acids, the contribution of the single functional groups to the whole stability of uranyl

species formed. In addition, using the stability data collected for the uranyl-ligand systems considered, the sequestering capacity of some classes of ligands towards uranyl was calculated in terms of $pL_{0.5}$, *i.e.*, the ligand concentration useful to bind at least 50% of the cation. A comparison of $pL_{0.5}$ of the most important classes of ligands considered was made to point out the different effectiveness in the UO_2^{2+} sequestration by the different ligands which can be present in multi-component solutions as natural waters and biological fluids. Finally, some considerations are reported about the different experimental techniques employed to study the complex formation in solution.

1. Introduction

The variety of human activities in using uranium for civilian, nuclear and war purposes leads to a wide diffusion of this element in the environment, producing a great concern for peoples and governments, owing to its radiological and toxicological effects [1-4]. For this reason, several research groups have been stimulated, for many years, to investigate the chemistry and toxicology of uranium in all its chemical forms in order to assess the potential chemical and radiological risk for the environment [5-9] and human health [10-13], paying particular attention to the risk resulting from the military use of depleted uranium (DU) [14-16]. The distribution and fate of uranium in the environment have been considered in the speciation studies of radionuclides [9, 17] and actinide elements [18, 19]. General information on the chemistry of uranium and its speciation in soils and sediments was reported in a recent article by Kelly [20]. Specific studies on the uranium speciation in soils and sediments, with particular reference to the uranium transport from mines and waste nuclear repositories, were carried out with the aim i) to characterize, by means of instrumental analytical techniques, the presence of natural and depleted uranium as a function of soil particles size [21-23], ii) to evaluate the kinetics of sorption and desorption of the element at the water-solid interface [24, 25], iii) to check the mobility through the surface systems [26], iv) to investigate the absorption and bioaccumulation by plants [27]. In all these studies, of relevant importance is the chemical composition of the soils under investigation where the presence of organic matter and living organisms can influence strongly the mobility and the bioavailability of uranium [28-32]. Since the mobility and transport of uranium in soils occurs *via water* [33], it is of great importance to investigate the aqueous chemistry of this element and its speciation in natural waters.

In the aquatic systems, the chemistry of U(VI) in oxidizing conditions is dominated by the presence of the dioxouranium(VI) cation (uranyl, UO_2^{2+}), which behaves as strong acid, in a Lewis acidity

scale, and shows high capacity of interacting with a variety of organic and inorganic ligands to form complex species of different stability. According to the predominant chemical behaviour of uranyl as “hard” cation, like other ions of actinide series, it binds inorganic oxygen donor ligands strongly. Interactions with inorganic oxygen donor ligands such as phosphate(V), vanadate(V), silicate and arsenate(V), largely of geochemical interest, are so strong as to lead to the formation of highly insoluble species [34] such as, for example, Autunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{--}12\text{H}_2\text{O}$ and the Uranophane $\text{Ca}(\text{UO}_2\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$ which is, probably, the most abundant uranyl silicate material and the most common uranium(VI) mineral together with the uranium(IV) oxide (Uraninite, UO_2) in the terrestrial crust [16]. Interaction of UO_2^{2+} with oxygen donor organic ligands were widely investigated, oxygen donor groups being present in most of naturally occurring organic compounds, like carboxylic and amino carboxylic acids, lipids, (poly)phenols, acidic (poly)saccharides, humic substances, etc. Uranyl undergoes strong hydrolysis with the formation of mono and polynuclear species that, in absence of strong precipitating agents (phosphate or carbonate) or strong complexing agents, dominates the chemistry of uranium(VI) in aqueous solution. Despite its prevalent “hard” ion behaviour, several investigations show a good tendency of UO_2^{2+} to react also with nitrogen and sulfur donor ligands, showing a partial “soft” behaviour. The simultaneous presence in natural waters of other metal ions [35] and different oxygen, nitrogen and sulfur donor ligands, which can compete among them in the UO_2^{2+} coordination [36], leads to a very complicated speciation picture of uranyl in such multi-component aqueous systems. Moreover, the soluble hydrolysis products of UO_2^{2+} have a great influence on the species distribution, in particular in the pH range up to 7, especially when the stability of complex species formed by the interaction with inorganic and organic ligands is not sufficient to fully suppress the hydrolysis. In this case, mixed hydrolytic species can be formed, especially in the presence of low reacting inorganic ligands [37], adding further complications to the speciation studies. On the other hand, it was shown that strong interactions of organic ligands with uranyl can enhance the solubility of uranium(VI) compounds favoring their mobility in the aquatic environment [38]. The complexation of actinides, with particular reference to uranium, with different organic and inorganic ligands in solution has been studied since the beginning of the development of nuclear energy, as documented by numerous articles and compilations [39-43].

To assess the chemical speciation model for UO_2^{2+} in aquatic systems and to define quantitatively the species distribution, reliable thermodynamic stability data are needed for the hydrolysis and interaction of UO_2^{2+} with the different organic and inorganic ligands in the pH range and at the ionic strength values and medium composition of natural aquatic systems. In this light and with the aim to give a survey, as updated as possible, of complex formation of dioxouranium(VI) for a

correct speciation of this cation in natural fluids, we will examine here the thermodynamic stability data reported in the literature for the formation of complex species of uranyl in aqueous solution with the following inorganic and organic ligands:

a) inorganic ligands: hydroxyl (water), chloride, fluoride, sulfate, carbonate and phosphate; interaction with chloride and sulfate simultaneously present in the aqueous solution will be examined by using a multi-component ionic medium representative of the inorganic major composition of sea water; b) low molecular weight organic ligands: carboxylates, amines, amino carboxylates (including amino acids), diphosphonates, mercapto and sulfonic ligands, nucleotides; c) high molecular weight organic ligands: polyacrylates, fulvic and humic acids, polyamines.

Since the aim of this review is to provide a general speciation picture of uranyl in natural fluids, the thermodynamic stability data for dioxouranium(VI) complexes in aqueous solution with all the above cited ligands will be analyzed, where possible, with regards to ionic strength, medium composition, pH of formation and temperature. Particular attention will be paid in the examination of the stability data, when sufficiently homogeneous, to find trends of stability for different ligands of the same class and of different classes. In some cases, general empirical equations will be proposed for classes of ligands, which allow us to roughly estimate the formation constant values for ligands not directly studied.

Most of the formation constants collected in this review were determined by means of the classical potentiometric, spectrophotometric and distribution measurements. Since the speciation proposed on the basis of these techniques, in particular for very complicated chemical systems, may be not unequivocal in some cases, we have also considered some reports coming from the use of other techniques (complementary with respect to the above ones), to point out the relevance of synergic contribution which further improve the solution of speciation problems.

2. Interaction of dioxouranium(VI) with inorganic ligands

2.1. Hydrolysis

Dioxouranium(VI) undergoes hydrolysis from pH~3.5-4 with the formation of several $(\text{UO}_2)_p(\text{OH})_q^{(2p-q)}$ species. The formation percentage and the type of hydrolytic species is strongly dependent on the concentration of UO_2^{2+} . In general mononuclear species are prevalent at low concentration ($< 1 \text{ mmol L}^{-1}$) while polynuclear complexes are formed at higher concentration. In particular, the simple $\text{UO}_2(\text{OH})^+$ hydrolytic product is found in very dilute solutions ($\ll 1 \text{ mmol L}^{-1}$). Many studies were devoted, in the past century, to the identification of the different hydrolyzed

UO_2^{2+} species formed in aqueous solution, and to determine their relative equilibrium constants. In this review we will report the constants relative to the equilibrium



The work done in this field was reviewed by Baes and Mesmer [43] and in the NEA reports [39, 44]. Critical values of stability constants are also reported in the NIST database [45]. In the oldest review, dating back 1976, only one mononuclear species, $(\text{UO}_2)(\text{OH})^+$, and three polynuclear species, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^+$ were considered, and the relative hydrolysis constants were reported. The trinuclear hydrolytic product $(\text{UO}_2)_3(\text{OH})_4^{2+}$ was reported to be present only in chloride solutions, being stabilized by the formation of a fairly stable Cl^- - $(\text{UO}_2)_3(\text{OH})_4^{2+}$ ion pair [46, 47].

Palmer and Nguyen-Trung [48] conducted potentiometric measurements at 0.1 mol kg^{-1} in tetramethylammonium trifluoromethanesulfonate in a wide range of concentrations and pH, and identified the species: $(\text{UO}_2)_2(\text{OH})_2^{2+}$; $(\text{UO}_2)_3(\text{OH})_4^{2+}$; $(\text{UO}_2)_3(\text{OH})_7^-$; $(\text{UO}_2)_3(\text{OH})_8^{2-}$ and $(\text{UO}_2)_3(\text{OH})_{10}^{4-}$, reporting also the relative hydrolysis constants. The same authors, together with other coworkers [49], confirmed the above speciation and, in addition, proposed the formation, at $\text{pH} > 2$, of the species $(\text{UO}_2)_3(\text{OH})_{11}^{5-}$ and $(\text{UO}_2)(\text{OH})_4^{2-}$, using Raman spectra. These authors affirm that the species $(\text{UO}_2)_3(\text{OH})_7^-$ is dominant over most of the pH range from 4.5 to 12.8.

In Ref.[44], authors analyzed carefully the literature reporting studies on the uranyl hydrolysis and selected the most reliable speciation models together with the critical values of hydrolysis constants (more recently, this NEA report was updated [39]). In addition to the species reported by Baes and Mesmer [43], the formation of the mononuclear species $(\text{UO}_2)(\text{OH})_i$, $i = 1 \dots 4$, was proposed together with the polynuclear species $(\text{UO}_2)_3(\text{OH})_7^-$ and the $(\text{UO}_2)_4(\text{OH})_7^+$. The NIST database [45] takes into account only the first mononuclear, the dinuclear and the trinuclear $(\text{UO}_2)_3(\text{OH})_5^+$ species. In Table 1, we show the values proposed by the above reviews, that include almost all the literature until the end of the last century. More recently, some results were reported confirming substantially the speciation scheme already proposed. Among these, we selected the results of three investigations [47, 50, 51], reported in Table 1.

The body of data in Table 1 can be summarized as follows:

1. The uranyl cation forms several mono- and polynuclear species whose stability is fairly high. For example, the first mononuclear product shows a stability, according to the formation reaction: $\text{UO}_2^{2+} + \text{OH}^- = (\text{UO}_2)(\text{OH})^+$, $K^{OH} = 10^{8.8}$. Moreover the stability of the mononuclear species can be modeled by the empirical equation (with β^0 we indicate the

equilibrium constant at infinite dilution and in parentheses we report the confidence interval value associated to the equilibrium constant)

$$-\log \beta_q^0 (\pm 0.3) = 2.90 + 0.82 q (1+2q) \quad (2)$$

2. An evident predominance of polynuclear species can be observed. In fact, the dimerization constant $K_D = \beta_{22} / \beta_{11}^2$ is quite high. By considering the values of β_{11} and β_{22} in Table 1, we have $\log K_D \geq 4.8$.
3. The formation of trinuclear and tetranuclear species with $q = 7$ can be accepted in a complete speciation model, in particular the trinuclear species, for dilute uranyl concentrations.
4. For the formation of polynuclear species, it is also possible to write an empirical equation, as a function of the stoichiometric coefficient:

$$-\log \beta_{pq}^0 (\pm 0.4) = 3.92 - 7.88 p + 6.80 q + 3.98 p/q \quad (3)$$

The dependence on ionic strength and on ionic medium was widely studied [39, 44, 47, 51]. In general, the results in NO_3^- and ClO_4^- are fairly similar, whilst hydrolysis data in chloride media are quite different, owing to the formation of ion pairs, of both UO_2^{2+} and $(\text{UO}_2)_3(\text{OH})_4^{2+}$, with Cl^- . The specific interaction coefficients, of UO_2^{2+} with Cl^- , NO_3^- and ClO_4^- , were reported in the NEA publications [39, 44, 50]. The parameters for the Pitzer equation [52] were calculated by Gianguzza *et al.* [46]. Measurements performed in synthetic sea water [46] and in sulfate aqueous medium allowed one to calculate all the Pitzer parameters we need to model the hydrolysis of uranyl in marine environment.

The dependence on temperature of hydrolysis constants and the enthalpy changes for the hydrolysis was studied not extensively, in comparison with the equilibrium constants investigations. In addition to the reviews already cited [39, 44], in the last decade, only some papers report ΔH values [51, 53]. Some ΔH of hydrolysis are reported in Table 1. Note that no reliable value is shown for the mononuclear species with $q > 1$, and for the species $(\text{UO}_2)_4(\text{OH})_7^+$. Nevertheless, by analyzing the available enthalpy change values for the hydrolysis of UO_2^{2+} , it was possible to find the empirical equation:

$$\Delta H_{pq} (\pm 4) = 33.2 - 20.15 p + 29.5 q \quad (4)$$

useful to estimate also unknown ΔH_{pq} values. Suggested values for the $\log \beta_{pq}^0$, ΔG_{pq}^0 , ΔH_{pq}^0 and $T\Delta S_{pq}^0$ values are reported in Table 2. Sometimes, rough values with confidence interval $>0.5 \log$

units were calculated in different ways: i) by weighted average of reported data (when more than two values are available), or ii) by using the few literature data coupled with the results of the empirical equations (2)-(4).

The neutral species $(\text{UO}_2)(\text{OH})_2^0$ is characterized by a quite low solubility, with $\log K_{s0}^0 = -23.2 \pm 0.4$ (Schoepite). Different solid phase structure imply different $\log K_{s0}^0$ values, and for the amorphous phase $\log K_{s0}^0 \cong -22.8$ [39]. The formation of $\text{UO}_2(\text{OH})_{2(s)}$ starts at $\text{pH} \sim 3.8$ for uranyl concentration 0.001 mol L^{-1} , and at $\text{pH} \sim 5$ for $10^{-4} \text{ mol L}^{-1}$; at concentrations $\leq 10^{-7}$ soluble hydrolytic species are prevalent.

Natural aquatic systems contain generally several metal ions and ligands, in particular when dealing with waste water. Therefore, the possible formation of mixed species must be investigated. To analyze the formation of hetero-metal polynuclear hydrolytic species (mixed-metal hydrolysis), the complexes $\text{UO}_2^{2+}/\text{Cu}^{2+}$, $\text{UO}_2^{2+}/(\text{C}_2\text{H}_5)_2\text{Sn}^{2+}$ [54] and $\text{UO}_2^{2+}/\text{Cd}^{2+}$ [55] were studied experimentally. For all the three mixed metal systems hetero-metal species are formed, showing a stability higher than that statistically predicted. The extra-stability of charged mixed-metal species causes a significant enhancement of the percentage of hydrolyzed metal cations.

The hydrolysis of the dioxouranium(VI) ion was also recently studied in a number of binary electrolytes (LiCl , NaCl , MgCl_2 , CaCl_2 and Na_2SO_4) and in some mixtures of these electrolytes, as well as in artificial sea water, at different ionic strengths [46]. This investigation reports both the apparent hydrolysis constants at different salinities (5 to 45‰), and the interactions of UO_2^{2+} and the different cationic and anionic hydrolytic species with anions and cations of the supporting electrolytes.

2.2. Fluoride and chloride

Dioxouranium(VI) cation forms quite stable complexes with fluoride anion, of the type $(\text{UO}_2)\text{F}_i^{(2-i)}$. In the reviews of NEA [39, 44], some $\log \beta_i$ values were selected: $\log \beta_1^0 = 5.16 \pm 0.06$; $\log \beta_2^0 = 8.83 \pm 0.08$; $\log \beta_3^0 = 10.90 \pm 0.10$ and we think that these are the best ones till now available. Recently, Tian and Rao [56] reported $\log \beta_1^0 = 5.20 \pm 0.07$, $\log \beta_2^0 = 8.74 \pm 0.07$ and $\log \beta_3^0 = 11.25 \pm 0.09$, in quite good agreement with previously proposed values. Ahrlund and Kullberg [57] measured the enthalpies of formation of the $(\text{UO}_2)\text{F}_i^{(2-i)}$ species in sodium perchlorate medium at $t = 25 \text{ }^\circ\text{C}$ by direct calorimetric titrations obtaining: $\Delta H_1^0 = 1.7 \pm 0.08$, $\Delta H_2^0 = 0.4 \pm 0.17$ and $\Delta H_3^0 =$

0.25 ± 0.25 and $\Delta H_4^0 = -2.06 \text{ kJ mol}^{-1}$; these results reveal that the first three species are formed in endothermic reactions and that the complex formation for this system depends on the large gain of entropy involved. Recently, Tian *et al.* [56] performing spectrophotometric (at different temperatures) and calorimetric measurements calculated the following enthalpy changes: $\Delta H_1^0 = 2.8 \pm 0.4$, $\Delta H_2^0 = 5.2 \pm 0.8$ and $\Delta H_3^0 = 3.4 \pm 1.1 \text{ kJ mol}^{-1}$, at $I = 0 \text{ mol kg}^{-1}$. Other species, with $i > 3$, were proposed, but are not considered in this review since they have little relevance in the speciation of natural fluids. Attempts were also made to find the formation of mixed species with OH⁻ [58], but only upper limits for the formation constants of $(\text{UO}_2)_2(\text{OH})_2\text{F}^+$ and $(\text{UO}_2)_3(\text{OH})_3\text{F}$ complexes were reported.

Chloride complexes of UO_2^{2+} are quite weak and it is difficult to discriminate between activity and complexation effects. In the NEA reviews [39, 44] two complexes $(\text{UO}_2)\text{Cl}_i^{(2-i)}$ ($i = 1, 2$) were selected, with $\log \beta_1^0 = 0.17 \pm 0.02$ and $\log \beta_2^0 = 1.1 \pm 0.4$. The uncertainty in $\log \beta_1^0$ seems too low and we think the values recently proposed are more reliable [46]: $\log \beta_1^0 = 0.4 \pm 0.2$, $\log K_{(\text{UO}_2)_3(\text{OH})_4\text{Cl}^+}^0 = 1.6 \pm 0.2$ [equilibrium: $(\text{UO}_2)_3(\text{OH})_4^{2+} + \text{Cl}^- = (\text{UO}_2)_3(\text{OH})_4\text{Cl}^+$].

Recently, Soderholm *et al* [59] studied the coordination of UO_2^{2+} with chloride by high energy X-ray scattering (HEXS) and from the studies performed on a series of solution at different chloride concentrations, they observed that chloride forms only inner-sphere complexes with uranyl, replacing inner-sphere waters. From solutions prepared at constant ionic strength ($I = 5.3 \text{ mol kg}^{-1}$), these authors also calculated the following stability constants: $\beta_1 = 1.5 (\text{mol kg}^{-1})^{-1}$; $\beta_2 = 0.8 (\text{mol kg}^{-1})^{-2}$, $\beta_3 = 0.4 (\text{mol kg}^{-1})^{-3}$ and the number of water molecules coordinated to each complexes. A review on the effect of temperature on UO_2^{2+} complexation with F^- , SO_4^{2-} , $\text{HPO}_4^-/\text{H}_2\text{PO}_4^-$, was recently published [60].

2.3. Sulfate

Fairly stable species are formed by UO_2^{2+} in the presence of SO_4^{2-} in acid solutions resulting from underground uranium ore leaching or from remediation of leaching sites. For the species $(\text{UO}_2)(\text{SO}_4)_i^{(2-2i)}$, the NEA reviews [39, 44] report the proposed values at $t = 25 \text{ }^\circ\text{C}$: $\log \beta_1^0 = 3.15 \pm 0.02$ and $\log \beta_2^0 = 4.14 \pm 0.07$.

Among all the published data on the coordination of UO_2^{2+} with SO_4^{2-} , a significant contribution to better understand the probable stoichiometry of the complexes was obtained from the Raman investigation performed by Nguyen-Trung *et al.* [61]; these authors observed the formation of the

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$(\text{UO}_2)(\text{SO}_4)^0$, $(\text{UO}_2)(\text{SO}_4)_2^{2-}$ and $(\text{UO}_2)(\text{SO}_4)_3^{4-}$ species. In particular the first one is the predominant species in acidic solution, and the continued presence of the last one indicates that the highest coordination number of sulfate ligand is probably 3, consistent with the strong bidentate bonding to the uranyl center. There is, in the literature, a discussion about its existence of the $(\text{UO}_2)(\text{SO}_4)_3^{4-}$ species, and some authors such as Vopálka *et al.* [62] and Gál *et al.* [63] consider the $(\text{UO}_2)(\text{SO}_4)_3^{4-}$ species only as a minor component. This was also recently confirmed by Henning *et al.* [64], who studying aqueous solutions with UO_2^{2+} -sulfate complexes by EXAFS and HEXS, observed the formation only of mono- and bidentate species.

More recently, from potentiometric measurements in Na_2SO_4 and in the mixtures $\text{Na}_2\text{SO}_4/\text{NaCl}$ and $\text{Na}_2\text{SO}_4/\text{NaNO}_3$, $\log \beta_1^0 = 3.4 \pm 0.2$ and $\log \beta_2^0 = 4.6 \pm 0.2$ were obtained [46]. Mixed sulfate/ OH^- complexes are formed, as reported in some papers [39, 44], but the stoichiometry is still uncertain. Provisionally we propose the following speciation, together with overall formation constants at infinite dilution [46]: $\log \beta_{(\text{UO}_2)(\text{SO}_4)^0} = 3.40 \pm 0.07$; $\log \beta_{(\text{UO}_2)(\text{SO}_4)_2^{2-}} = 4.62 \pm 0.06$; $\log \beta_{(\text{UO}_2)(\text{OH})(\text{SO}_4)^-} = -1.90 \pm 0.12$; $\log \beta_{(\text{UO}_2)_2(\text{OH})_2(\text{SO}_4)^0} = -2.00 \pm 0.12$; $\log \beta_{(\text{UO}_2)_3(\text{OH})_4(\text{SO}_4)^0} = -6.89 \pm 0.13$; $\log \beta_{(\text{UO}_2)_3(\text{OH})_5(\text{SO}_4)^-} = -11.87 \pm 0.15$ (all the parameters are expressed with the confidence interval reported in the original manuscript).

Recently, a review on the dependence of the stability of UO_2^{2+} - SO_4^{2-} complexes on temperature was published [60].

2.4. Carbonate

The data reported for the carbonate complexes were analyzed in the NEA compilations [39]. The selected values at zero ionic strength and at $t = 25$ °C are collected in Table 3.

The literature reports quite different speciation models, for the uranyl carbonate system, and the formation of a minor mixed hydroxide carbonate species was proposed in a previous review [44]. In particular for the formation of the complex $(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$, according to the reaction $2\text{UO}_2^{2+} + \text{CO}_{2(\text{g})} + 4\text{H}_2\text{O} = (\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$, the value at $t = 25$ °C of $\log K = -19.42 \pm 0.11$, at $I = 0.5$ mol L^{-1} was reported.

As well as other inorganic ligands, also in the case of carbonate are there many discussions on the effective stoichiometry of the uranyl/carbonate complexes. For example Bernhard *et al.* [65] from Time Resolved Laser induced Fluorescence Spectroscopy (TRLFS), reported the existence of a neutral species, namely $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$, proposing an average overall formation constant of $\log \beta_{213} = 30.55 \pm 0.25$. This is in accordance with the value calculated from Kalmykov *et al.* [66] who

report $\log \beta_{213} = 29.8 \pm 0.7$ calculated at infinite dilution, by using the SIT theory. Successively Geipel *et al.* [67] studied the interaction of Mg^{2+} , Sr^{2+} and Ba^{2+} with the uranyl tricarbonate complex and determined the stoichiometry and the stability constants of such complexes. These authors prepared the stock solutions at pH and CO_3^{2-} concentration values, at which the $\text{UO}_2(\text{CO}_3)_3^{4-}$ is the only species in the initial solution and, after addition of the solutions containing the alkaline earth cations, observed the formation of two complex species, namely the $\text{MeUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Me}_2\text{UO}_2(\text{CO}_3)_3^0_{(\text{aq})}$ ($\text{Me} = \text{Mg}^{2+}$, Sr^{2+} or Ba^{2+}). The formation of the last complex influences the speciation of uranium species distribution in the pH range from 6.0 to about 10.0 and becomes the most important species in the solution. This is of great importance for the environmental behaviour and the mobility of uranium under natural conditions.

Other authors, such as Allen *et al.* [68] reported the formation of some other polynuclear species, such as the $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ determined by NMR, Raman, EXAFS and X-Ray diffraction [68] and the $(\text{UO}_2)_3(\text{OH})_3\text{CO}_3^+$. Moreover, Ciavatta *et al.* [69] report that, besides the species already cited, in the vicinity of the precipitation point of the uranyl/carbonate species, a species having a larger number of metal ions is formed, with a probable stoichiometry of $(\text{UO}_2)_{11}(\text{OH})_{24}(\text{CO}_2)_6^{2-}$.

Recently, a study for the influence of the temperature (in the range 253-343 K) on the carbonate complexation of uranium(VI) was published [70].

2.5. Phosphate

The formation of insoluble and slightly soluble uranyl/phosphates is important in the technology of uranium production, especially for low-grade uranium phosphate ores and in fuel reprocessing.

Many authors investigated the formation of uranyl phosphate complexes, but there is still quite a significant disagreement both in terms of speciation of the system, and for the stability of the species. The NEA analyzed the data published up to 2003 [39], and the selected values at zero ionic strength are reported in Table 3 together with those of the carbonate system. Recently some other interesting studies were published on the uranyl/phosphate system [71-75]. In some of these studies carried out by TRLFS investigation, also at high temperature and pressure [71, 72], the speciation model reported in Table 3 was confirmed.

Vazquez *et al.* [73] studied by EXAFS, the solubility and association of uranyl also with polyphosphate; in contrast to uranyl phosphate, the uranyl/polyphosphate complex is soluble over a wide pH range and the solubility and the structure differ with the experimental pH, suggesting that at least two different types of complexes are generated, namely a monodentate uranyl species with phosphate at $\text{pH} < 6$, and bidentate at higher pHs.

Savenko [74] studied the solubility of UO_2HPO_4 in sea water at a salinity of 35‰; the author observed that the solubility of the salt increases nonlinearly with decreasing acidity due probably to the formation of hydroxo, carbonate complexes and at $\text{pH} > 7.5$, dissolves congruently.

Sowder *et al.* [75] studied the dissolution of different $\text{UO}_2\text{-Ca-PO}_4$ minerals, when in contact with different extractants, and observed significant variations in the rate and extent of the dissolution among the minerals. Some of them, such as chernikovite $[(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}]$ and meta-autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ proved resistant to dissolution in non-carbonate systems, with dissolution half-times up to years when low concentration of extractant were used.

To show the relevance of uranyl inorganic species in a natural water, we report in Figures 1 and 2, two speciation diagrams concerning marine water (salinity 35 ‰). In the first one the real major composition of sea water was considered, whilst, in the second diagram, the addition of phosphate ($5 \cdot 10^{-5} \text{ mol L}^{-1}$) was taken into account. The relative calculations were performed by using the sea water model already reported [76-78] and the equilibrium constants for the hydrolysis and for the inorganic complexes of UO_2^{2+} selected in this review. Both Figures indicate the predominance of carbonate species (in the absence of phosphate) or carbonate and phosphate complexes, in the pH range of interest of marine water ($\text{pH} \sim 8$); the formation percentage of both carbonate and phosphate species are dependent on pH; in particular the phosphate ion sequester almost totally UO_2^{2+} up to $\text{pH} \sim 7$, while the formation percentages of the carbonate species become significant at $\text{pH} > 7.2$. Fluoride, chloride and sulfate species must be considered only in the acidic range.

3. Interaction of dioxouranium(VI) with organic ligands

3.1. Carboxylates

Literature reports several data on the interaction of uranyl with different carboxylic ligands [61, 79-105], published some decades ago. Often the aim of these studies is to identify model molecules able to simulate the behaviour and the thermodynamic properties of the organic matter. Since a large proportion of soil organic matter consists of quite complex polymeric molecules (humic matter), with aromatic rings containing carboxylic and phenolic groups as principal chelating groups, oxygen donor ligands can be used for modelling purposes. In the past, for example, phthalate, salicylate and dihydroxybenzoate were used as model molecules.

However, unfortunately, the limit of a large part of the investigations reported in the literature is that in only few cases a systematic study of the dependence of thermodynamic parameters on ionic strength, temperature or on the experimental conditions was carried out. In many cases, the

experimental investigations are limited to the determination of the structure of the complex formed in the solid phase or in solution, without reporting the values of stability constants. This implies that it is very difficult to make comparison among the different papers. Moreover the literature information on the interaction of uranyl with carboxylate ligands often refers to a restricted pH range, generally at low pH values, where the influence of the hydrolytic reactions is neglected in order to simplify the studies. This condition limits the application of the results to natural systems. The results reported by Berto *et al.* and Crea *et al.* [106-111], Jiang *et al.* [90] and Moore *et al.* [82] are worthy of mention, since they studied the interaction of uranyl with carboxylate in different conditions of ionic strength, ionic media and temperature up to high pH values, by using different experimental techniques and giving structural information to identify the coordination modes of the complexes in solution. Moore *et al.* [82] and Crea *et al.*[111] reported reliable stability constant values for the uranyl-acetate system, studied at different ionic strengths (NaCl_{aq}). Crea *et al.*[111] carried out a critical analysis of literature data of the uranyl-acetate complexes and proposed recommended (in some cases tentative) $\log\beta_{\text{pqr}}$ values for the formation of complexes. Moreover, for the mixed species $(\text{UO}_2)(\text{ac})_3(\text{OH})^{2-}$, firstly reported by Jiang *et al.*[90] using EXAFS technique, Crea *et al.* [111] calculated the corresponding formation constant value, at different ionic strengths. Jiang *et al.*[90], reported also the enthalpy and entropy changes for the different complexes (at 1.05 mol kg^{-1} in NaClO_4), determined by calorimetric titrations; the positive $\Delta H/\text{kJmol}^{-1}$ values indicate that the stability of the species increases with the temperature. Other significant comparison can be made only for few ligands, such as succinate and malonate [84-89, 94-96, 98, 106], whilst for the others carboxylic ligands, the no homogeneity of the thermodynamic data and of the experimental conditions used does not allow us to make significant comparisons.

Also in the case of the uranyl-malonate and uranyl-succinate systems, we may observe a substantial agreement between the different literature values, but only for the mononuclear simple species. On the contrary, few data can be found on the formation of mixed hydrolytic species and on the dependence on ionic strength. Berto *et al.*[106] analysing the results of a systematic study on the speciation of uranyl with some linear dicarboxylic ligands, $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$ with $n = 1-7$, observed that different carboxylates have different speciation models and formation constants (at the same ionic strength). Moreover the speciation models are fairly different in $\text{KNO}_{3\text{aq}}$ and NaCl_{aq} [106]. The first issue simply relies to the length of alkyl chain interposed between the two carboxylic groups. The most favourable structure is offered by malonate, which forms very stable rings; this allows the formation of other species. For example, in the case of azelate (aze, $n = 7$) system the sharp separation of carboxylic groups allows the dimeric species $(\text{UO}_2)_2(\text{aze})_2^0$ to be formed. Moreover the formation of protonated, monodentate complexes is favoured for higher

values of n , that means pK^H_1 and pK^H_2 values close to each other. The differences relative to the second issue are due to three factors, namely, i) the different extent of interaction of K^+ and Na^+ with carboxylic anions ($Na^+ > K^+$); ii) the different strength of ion pairs formed by UO_2^{2+} and Cl^- or NO_3^- ($Cl^- > NO_3^-$); iii) the shorter pH range in KNO_3 , before precipitation of insoluble species.

Kirishima *et al.* [112] determined the thermodynamic quantities (ΔG , ΔH and ΔS) of uranyl complexation with 5 dicarboxylates ($HOOC-(CH_2)_n-COOH$ with $n = 0-4$) having different carbon chain lengths, and showed an interesting tendency, that is $-\Delta H$ decreased and $T\Delta S$ increased systematically with increasing the length of the carbon chain; moreover the thermodynamic quantities indicated that these complexation, as well as for the other uranyl-carboxylate complexes, are mainly driven by the entropy. These authors [113], performed similar investigation in $NaClO_4$ at $I = 0.1 \text{ mol L}^{-1}$ on some monocarboxylic acids, (such as, formic, acetic, glycolic and propionic acids) obtaining similar evidences.

Recently similar evidence was obtained studying the interaction of uranyl with other polycarboxylate such as: diglycolic acid (oda) and diethylenetrioxydiacetic acid (toda) [109], 1,2,3-propanetricarboxylates (tca) [108], 1,2,3,4-butanetetracarboxylate (btc) [107], 1,2,3,4,5,6-benzenehexacarboxylate (mellitate, mlt) [110].

Collecting all the literature data on the interaction of UO_2^{2+} with carboxylic ligands (see Table 1S of Supplementary Information) and performing suitable calculations, it is possible to observe that the formation constants values are a linear combination of the stoichiometric coefficients of the complexes and of the ligand structures. For example, taking only into account the stability constants of the ML ($M = UO_2^{2+}$ and $L = \text{generic carboxylate}$) complex species obtained from the interaction of UO_2^{2+} with the most common carboxylic ligands [acetate (ac), malonate (mal), oxalate (ox), succinate (suc), azelate (aze), diglycolic acid (oda) and diethylenetrioxydiacetic acid (toda), 1,2,3-propanetricarboxylates (tca), 1,2,3,4-butanetetracarboxylate (btc), 1,2,3,4,5,6-benzenehexacarboxylate (mellitate, mlt), benzoate, formiate, etc.), it is possible to obtain an equation, valid for the carboxylic ligands not containing other potential binding sites, that allows one to describe the dependence of the stability constants on the number of the carboxylic groups (n) in the ligands and on the ionic strength (I):

$$\log\beta = p_1 \cdot n + p_2 \cdot n^2 - z^* \cdot DH + z^* \cdot n \cdot C \cdot I \quad (5)$$

where p_1 and p_2 are the empirical parameters for the dependence of the stability constant on n , whilst C is the parameter for the dependence of $\log\beta$ on I , respectively. $z^* = \sum z^2_{\text{reactants}} - \sum z^2_{\text{products}}$ (z = charge of the species) and DH is the Debye-Hückel term ($0.51 \cdot \sqrt{I} / (1 + 1.5\sqrt{I})$). The elaboration of

literature data gives: $p_1 = 3.26$; $p_2 = -0.27$; $C = 0.064$, with a confidence interval in $\log\beta$ of ± 0.3 . Obviously, this approach, as well as the next one, allows one to estimate rough values of the formation constants of complexes not experimentally obtained or lacking in the literature or not determined at the ionic strength of interest for our speciation model.

Similarly, by collecting all the literature stability constants values of the complexes formed by the interaction of UO_2^{2+} with several O-donor ligands, including oxalate and citrate complexes (see Table 1S of Supplementary Information) at different ionic strengths and in different ionic media. The stability constant values were processed with the following equation:

$$\log\beta_{pqr} = p_1 + p_2 \cdot n + p_3 \cdot p + p_4 \cdot q + p_5 \cdot r - \text{DH} \cdot z^* + C \cdot I \cdot z^* \quad (6)$$

applicable to all the different $\log\beta_{pqr}$ species of the uranyl-polycarboxylate complexes at different ionic strengths at $t = 25$ °C, where $p_1 = -8.60$ is the intercept, and $p_2 = 1.18$, $p_3 = 8.07$, $p_4 = 3.10$, $p_5 = 5.44$ are the empirical parameters dependent on: i) the number (n) of carboxylic groups in the ligand, ii) the stoichiometric indexes (p , q , r) of UO_2^{2+} complexes, iii) the ligand and H^+/OH^- in the complexes, respectively, while $C = 0.076$ takes into account the dependence of the stability constants on the ionic strength; all the parameters are expressed with a confidence interval in $\log\beta$ of ± 0.8 .

When considering the dependence on ionic strength of formation constants, one must take into account the different interacting abilities of different cations of various supporting electrolytes used in the original investigations (sodium, potassium and tetralkylammonium salts). In fact Na^+ and K^+ form weak ion pairs, of different stability [114] whilst X_4N^+ ($\text{X} = \text{CH}_3, \text{C}_2\text{H}_5$) are considered generally baseline supporting cations (not interacting). The use of different salts can give different results, in terms of formation constants, even at the same ionic strength.

Two relevant, and widely studied ligands are oxalate and citrate, discussed fairly extensively in the following sections.

3.2. Oxalate

In the large amount of literature reports on the interaction of uranyl with oxalate [87, 115-126], published since 1950 (see Table 1S of Supplementary Information) and collected recently by the NEA agency [39], the investigations were generally carried out at a single ionic strength value, or in a non-interacting ionic medium, such as NaClO_4 , and in the acidic region ($\text{pH} \leq 4.5$) where the formation of both simple and ternary hydrolytic species is avoided. The only new data available after the publication of this book are those reported by Crea *et al.* [127] and Manfredi *et al.* [128]

and Di Bernardo *et al.* [129]. Only Borkowski *et al.* [122, 124] and Crea *et al.* [127] extended the study to different ionic strength values in NaCl. The most of papers reports only the formation of the binary uranyl-oxalate species: $(\text{UO}_2)\text{ox}^0$, $(\text{UO}_2)(\text{ox})_2^{2-}$ and $(\text{UO}_2)(\text{ox})_3^{4-}$ [39, 87, 92, 115, 116, 119-124, 126], but since recently Manfredi *et al.* [128] and Crea *et al.* [127] carried out measurements up to the basic region and indicated the formation of some polynuclear ternary hydrolytic species as well. Havel *et al.* [118] introduced two new binary polynuclear species (whose existence is still in doubt), namely $(\text{UO}_2)_2(\text{ox})_3^{2-}$ and $(\text{UO}_2)_2(\text{ox})_5^{6-}$, as reported in studies performed by EXAFS [130].

Tentative comparison can be made only for the $(\text{UO}_2)(\text{ox})^0$, $(\text{UO}_2)(\text{ox})_2^{2-}$ and $(\text{UO}_2)(\text{ox})_3^{4-}$ species reported in [39, 87, 92, 115-128], the $(\text{UO}_2)(\text{ox})(\text{OH})^-$ species reported by Crea *et al.* [127] and Manfredi *et al.* [128] and the $(\text{UO}_2)_2(\text{ox})_5^{6-}$ reported by Crea *et al.* [127] and Havel *et al.* [118]. In the review published by the NEA [39] it is also proposed the formation of some ternary protonated species not considered in many other investigations. In Crea *et al.* [127] a calorimetric investigation on the uranyl-oxalate complexes was also performed; the results indicate that the entropic contribution is the predominant effect in the formation of the species. In this paper, the dependence of the stability constants on ionic strength was given, together with the specific ion interaction coefficient for each uranyl-oxalate species. These results, were more recently confirmed from the investigation carried out by Di Bernardo *et al.* [129] by spectrophotometric and calorimetric investigation at $I = 1.05 \text{ mol kg}^{-1}$ and $t = 10-70 \text{ }^\circ\text{C}$. Authors report that the complexation of uranyl with oxalate ion is exothermic at lower temperature, up to $t = 40 \text{ }^\circ\text{C}$, but becomes more negative at higher values due to the increasingly more positive entropy of complexation that exceeds the increase of the enthalpy of complexation.

Crea *et al.* [127] and Manfredi *et al.* [128], characterised by thermogravimetry the insoluble dioxouranium(VI)-oxalate species obtained at $I = 1.0 \text{ mol L}^{-1}$. Independently of the ionic medium, namely NaCl and NaClO_4 , authors proposed the formation of the $\text{Na}_4(\text{UO}_2)_2(\text{ox})_2(\text{OH})_4$ solid species.

In the speciation studies of the uranyl-oxalate system, Crea *et al.* [127] observed a regular trends between the stability constants of the simple $(\text{UO}_2)_p(\text{ox})_q^{(2p-2q)}$ and the number of coordinated sites; for example, if we consider $\text{UO}_2(\text{ox})^0$ to be bi-coordinated, $\text{UO}_2(\text{ox})_2^{2-}$ to be tetra-coordinated and $\text{UO}_2(\text{ox})_3^{4-}$ to be penta-coordinated, an almost perfect linear correlation is obtained, valid for the complexes at $I = 1.0 \text{ mol L}^{-1}$ in NaCl:

$$\log \beta_{pq} = 1.385 + 2.255 \cdot n \quad (R=0.9998) \quad (7)$$

where n is the number of coordination sites. Other factor can be taken into account to explain the stability of the different $(\text{UO}_2)_p(\text{ox})_q(\text{OH})_r^{(2p-(2q+r))}$ species: (a) the coordination number and number of chelate rings; (b) the complex charge; (c) the number of $-\text{OH}$ groups present in the molecule; and (d) the interaction of negatively charged complex species with the cation of the supporting electrolyte (medium stabilisation). Some empirical relationships were reported using these factors, for the ΔG^0 and $T\Delta S^0$ of UO_2^{2+} oxalate species formation [127].

3.3. Citrate

The interaction of dioxouranium(VI) with citrate was extensively investigated by several authors (see Table 1S as Supplementary Information) by using different instrumental techniques such as potentiometry, UV/Vis spectrophotometry, Raman spectroscopy, NMR, EXAFS, etc. [131-156]. Recently NEA [156] collected and analysed the data about the interaction of uranium with citrate, in order to give a specific database.

The tendency of uranyl to form quite stable chelate complexes with citrate is well recognized [137, 138, 157]. In particular dimeric and trimeric species are formed, in which bridging between metal ions occurs through carboxylates and hydroxylic groups of the ligand [158, 159]; this behaviour makes particularly difficult the speciation studies on this system. In fact, large discrepancies between literature data can be found, both in terms of speciation model and of stability constants values. For example, Vaňura *et al.* [146] proposed besides the $(\text{UO}_2)(\text{cit})^-$ and $(\text{UO}_2)_2(\text{cit})_2^{2-}$, also the $(\text{UO}_2)_2(\text{cit})_2\text{H}^-$ and the $(\text{UO}_2)_2(\text{cit})_2\text{H}_2^0$, formed at high H^+ concentration. Ohyoshi *et al.* [143] proposed approximate stability constants for only mononuclear protonated species, such as $(\text{UO}_2)\text{citH}^0$, $(\text{UO}_2)\text{citH}_2^+$ and $(\text{UO}_2)(\text{cit})\text{H}_3^{2+}$ in NaClO_4 0.1 mol L^{-1} , obtained at $\text{pH} = 2.2-2.9$. Rajan and Martell [157], by studying the dependence of stability constants on the concentration of the metal ion, in KNO_3 at $I = 0.1$ and 1.0 mol L^{-1} , observed that the $\log\beta_{\text{pqr}}$ values increase with increasing of the metal concentration; such trend indicates that polymerization reaction may be taking place in solution. Ohyoshi *et al.* [147], instead, studying the speciation of the uranyl-citrate system by cation exchange resin at different pH values, observed that the (apparent) stability constant value is a decreasing function of the pH.

Despite a lot of literature data published on the stability of the uranyl-citrate species, only few authors studied this system at different ionic strengths and in different ionic media [145, 157, 160]. Whilst Bronikowski *et al.* [145] report $\log\beta_{\text{pqr}}$ values only for the $(\text{UO}_2)(\text{cit})^-$, neglecting the formation of the most important $(\text{UO}_2)_2(\text{cit})_2^{2-}$ species, Berto *et al.* [160] studied the speciation of the system at different ionic strength values up to 1.0 mol L^{-1} , in NaCl and KNO_3 aqueous

solutions, up to $\text{pH} > 7$; the authors reported for the uranyl-citrate system the following speciation model: $(\text{UO}_2)(\text{cit})^-$, $(\text{UO}_2)_2(\text{cit})_2^{2-}$, $(\text{UO}_2)_2(\text{cit})_2(\text{OH})_2^{4-}$, $(\text{UO}_2)_2(\text{cit})_2(\text{OH})^{3-}$, $(\text{UO}_2)_2(\text{cit})(\text{OH})_2^-$, $(\text{UO}_2)_2(\text{cit})(\text{OH})^0$, $(\text{UO}_2)_3(\text{cit})_2(\text{OH})_5^{5-}$. The dependence of the stability constants on ionic strength was studied by means of a Debye-Hückel type equation [161, 162] and of the Specific Ion Interaction Theory approach (SIT) [163-167]. A similar treatment, as regards the dependence of stability constants on ionic strength, was performed in the NEA collection, but only for the $(\text{UO}_2)(\text{cit})^-$, $(\text{UO}_2)(\text{cit})_2^{2-}$ and $(\text{UO}_2)(\text{cit})\text{H}^0$ species; here, the authors by using the selected stability constants and correcting their values for the interaction of the metal ions with the anion of the supporting electrolyte (Cl^- or NO_3^-), calculated the specific interaction coefficient of each species. The magnitude of the correction is not large as compared to the estimated uncertainties of the values; due to the scarceness of reliable data, this collection assigns larger uncertainties to the values obtained from the fitting procedures

Taking into account the quite different experimental conditions used in the different investigations, the data reported by Berto *et al.* [160], Rajan *et al.* [157], Ohyoshi *et al.* [143] and Bronikowski *et al.* [145] for the $(\text{UO}_2)(\text{cit})^-$ species and by Berto *et al.* [160], Feldman *et al.* [137], Rajan *et al.* [157], Markovits *et al.* [168] and Li *et al.* [142] for the $(\text{UO}_2)_2(\text{cit})_2^{2-}$ species, at $I \sim 0.1$ and 1.0 mol L^{-1} in different ionic media, can be considered comparable among them. Other studies reported in the literature [169, 170] reveal the tendency of uranyl to form also mixed-metal complex with indium $(\text{UO}_2)\text{InL}_2$ where L is cit^{3-} , malate $(\text{OOCCH}_2\text{CH}(\text{OH})\text{COO}^{2-})$ and tartrate $(\text{OOCCH}(\text{OH})\text{CH}(\text{OH})\text{COO}^{2-})$, and with other metal ions [170].

3.4. Amines

An accurate examination of the literature shows that very few authors paid attention to the study of the interaction between uranyl and ligands containing only nitrogen donors. In this connection, Jarvis *et al.* [171] reported the formation constants of uranyl complexes with long chain synthetic nitrogen ligands (only containing, in addition, some alcoholic groups), which have no relation with natural waters or biological fluids. More interesting for this review are, on the contrary, the reports of Crea *et al.* [172], concerning the uranyl complexes formed with 1,2-diamino-ethane (ethylenediamine, en), 1,4-diamino-butane (putrescine, ptr), 1,5-diamino-pentane (cadaverine, cdv), *N*-(3-amino-propyl)-1,4-diamino-butane (spermidine, spd) and *N-N'*-bis(3-aminopropyl)-1,4-diamino-butane (spermine, sper), where en, ptr and cdv are diamines, spd is a triamine and sper a tetraamine. If L represents the amino ligand, the stability constants of the species formed in

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solution, at $t = 25$ °C and $I = 0.1$ mol L⁻¹, are $\log\beta_{110} = 9.88, 13.07$ and 12.20 for en, ptr and cdv, respectively, for the diamine complexes of the type $(\text{UO}_2)\text{L}^{2+}$ and $\log\beta_{11-1} = 3.21, 7.10$ and 6.38 for en, ptr and cdv, respectively, for diamines complexes of the type $(\text{UO}_2)\text{L}(\text{OH})^+$; for spd $\log\beta_{111} = 21.60$ and $\log\beta_{110} = 15.11$ ($(\text{UO}_2)\text{LH}^{3+}$ and $(\text{UO}_2)\text{L}^{2+}$ complexes, respectively) and for sper $\log\beta_{112} = 29.87$ and $\log\beta_{111} = 24.42$ ($(\text{UO}_2)\text{LH}_2^{4+}$ and $(\text{UO}_2)\text{LH}^{3+}$ complexes, respectively). In the same paper, the authors studied the interaction of UO_2^{2+} with poly(allyl)amine (15 kDa). Poly(allyl)amine (paam) forms four species, namely, $(\text{UO}_2)\text{L}^{2+}$, $(\text{UO}_2)\text{LH}_3^+$, $(\text{UO}_2)\text{LH}_2^{4+}$, and $(\text{UO}_2)\text{L}(\text{OH})^+$; the stability of the $(\text{UO}_2)\text{L}^{2+}$, $(\text{UO}_2)\text{LH}_3^+$ and $(\text{UO}_2)\text{L}(\text{OH})^+$ species at $I = 0.5$ mol·L⁻¹ is much higher than that at $I = 0.1$ mol·L⁻¹, while for the diprotonated complex species the stability is almost the same at the two ionic strengths. This behavior was explained by hypothesizing a stabilization of the cationic species by the anion of the supporting electrolyte.

It is clear that the stability of the above complexes strongly depends on the number of unprotonated amino groups in the ligand and also on the number of $-\text{CH}_2-$ which spaces them; in fact, for 110 species the highest stability is that of $(\text{UO}_2)(\text{spd})^{2+}$, while among the diamines the highest stability is that of $(\text{UO}_2)(\text{ptr})^{2+}$, in which three methylene groups space the two amino donors.

Taking into account the stability constants of the simple $(\text{UO}_2)(\text{amine})^{2+}$ species by Crea *et al.* [172], it is possible to obtain a simple linear relationship valid at $I = 0.1$ mol L⁻¹:

$$\log K = (5.8 \pm 0.5) \cdot n_N \quad (8)$$

(where n_N is the number of unprotonated amino groups), for the dependence of the $\log K$ values on the number of amino groups. If including the above hydroxylated complexes as well, another empirical correlation can be found at $I = 0.1$ mol L⁻¹ [172], regarding the values referred to $(\text{UO}_2)(\text{amine})^{2+}$ and $(\text{UO}_2)(\text{amine})(\text{OH})^+$ species. If d is the mean number of terms contributing to chelate ring(s), but the cation, and n_{OH} is the number of $-\text{OH}$ in the complex, an equation can be proposed of the type:

$$\log K(\pm 0.5) = p_1 \cdot n_N + p_2 \cdot (d - 6)^2 + p_3 \cdot n_{\text{OH}} \quad (9)$$

where $p_1 = 5.8$, $p_2 = -0.44$ and $p_3 = -0.40$. As an example, this equation enable us to calculate the formation constants, when precipitation does not allow a direct experimental determination.

3.5. Amino acids

A consistent part of coordination chemistry studies of uranium(VI) in natural aquatic systems and in biological fluids is focused on the interactions of UO_2^{2+} with amino acids. The interest in investigating these systems has to be attributed, in addition to the biological importance of amino acids, to the complexation capacity of these molecules which can react, in principle, as nitrogen and oxygen donor ligands, with the possible formation of chelate complexes. To assess the coordination patterns of the different amino acids (i.e., whether only one or both amino and carboxylic binding groups are involved in the coordination) and to determine quantitatively the thermodynamic stability data ($\log K$, ΔH , ΔS) of complex species formed by the interaction with uranyl ion, many articles [80, 89, 93, 102, 155, 173-217], reviews [218, 219] and compilations [220-223] have been published in the last 50 years. Stability data were reported in the general databases collecting stability constants values for complex species formation [40, 42].

A survey of literature data gives evidence for the formation of uranyl complex species with 28 amino acids and peptides (see Table 2S of the Supplementary Information). The most studied amino acids are glycine [93, 102, 179-181, 188, 193, 194, 204, 215, 217, 224], α -alanine [155, 180, 199, 203-205, 213, 216] and β -alanine [178-181, 201, 203, 204, 211, 213], aspartic acid [80, 176, 179, 186, 193, 206, 211, 212, 217, 225], glutamic acid [80, 186, 187, 193, 212] and serine [181, 182, 193, 201, 211, 215-217]. Moreover a sufficient quantity of data were found for valine [181, 199, 203, 205, 215, 226, 227], threonine [174, 199, 201, 208, 211], asparagine [174, 181, 193, 205, 217, 228] and cysteine [188, 189, 199-201, 216].

The stability of the complex species formed by amino acids with UO_2^{2+} ion depends on several factors such as i) the number of $-\text{CH}_2-$ groups between carboxylate and amino donors and the consequent formation of chelating ring(s) of different size and ii) the number, the type and the position of other binding groups in the substituent at the α -carbon.

In all the investigations the carboxylic groups were reported as active binding sites in the coordination, while there is no homogeneity in assessing the contribution of amino groups to the UO_2^{2+} - amino acid complexes formation. Lagrange *et al.* [193, 194] studied the interaction of UO_2^{2+} ion with several α -amino acids by potentiometry and UV-Vis spectroscopy. The results obtained, supported in some cases by IR experiments, confirmed that amino acids bind uranyl ion through both carboxylic and amino groups in equatorial position. The same conclusions were drawn by Cefola *et al.* [179], Tewari *et al.* [228] Sergeev *et al.* [211] and Sekhon *et al.* [210] assuming the substitution of the proton bound to amino group by uranyl even at $\text{pH} \leq 3.5$. On the contrary, Li *et al.* [93], Feldman *et al.* [80], Raghavan *et al.* [201] and, more recently, Moll *et al.* [155], and Gharib *et al.* [182] report the formation of $(\text{UO}_2)\text{LH}^{2+}$ and $(\text{UO}_2)\text{L}_2\text{H}_2^{2+}$ species in the acidic pH range, excluding the involvement of the amino group in the coordination. Structural investigations on

uranyl complexes with glycine and its –SH derivatives, carried out by X-ray crystallography and NMR spectroscopy [191], confirm that, in biological systems, amino acids bind uranyl preferentially by carboxylate groups.

Ramanujam *et al.* [204] reported $\log K$ values of the $(\text{UO}_2)(\text{HL})_2^{2+}$ complex species of α -, β - and γ -amino acids, pointing out that the destabilizing effect of the positively charged amino group on the stability of the complex species increases in the order: α -amino acid > β -amino acid > γ -amino acid. The same stability trend was found by Bismondo *et al.* [178] for different UO_2^{2+} complexes with α -, β - and γ -amino acids.

From a careful analysis of literature data a series of limits emerges: i) the main ionic medium used by authors was NaClO_4 and most of the results were obtained at a single ionic strength, usually 0.1 mol L^{-1} ; both these conditions are useless for speciation studies in natural systems; ii) only few authors report stability data at different ionic strengths [182, 184, 186, 208, 209]; iii) most of the data were obtained at a single temperature, usually $t = 25^\circ\text{C}$ or, in some case, at a temperature value between 20 and 35°C ; iv) quantitative data on the interaction of uranyl with amino acids were mostly obtained in a restricted pH range, often not over pH 4, and in many cases also neglecting the hydrolysis of uranyl. Only few authors made experiments at higher pH and included the hydrolytic species of uranyl in their complexation model. Dongre *et al.* [180] studied the interaction of UO_2^{2+} with glycine, α - and β -alanine and histidine by polarography in the pH range 4.8 – 5. The authors neglected the hydrolytic species of uranyl asserting that this approximation can be considered correct when the solution contains an excess of ligand ($10 \leq L : \text{UO}_2^{2+} \leq 35$). Szabó *et al.* [224] calculated the formation constant of the species $(\text{UO}_2)(\text{glycine})_2^0$ obtained by ^{19}F -NMR experiments in the pH range 2 - 8.5. The authors did not consider hydrolysis of UO_2^{2+} , which was avoided by using a second ligand (F⁻), that preferentially binds uranyl and, in presence of glycine forms ternary complexes. Gianguzza *et al.* [186] carried out a potentiometric study on the interaction of uranyl ion with aspartate and glutamate in the pH range 3.5 – 6, in NaCl, in the ionic strength range $0.1 - 1 \text{ mol L}^{-1}$. In this case the authors considered in their complexation model the hydrolytic species of uranyl and underlined that these species are already formed in solution at pH = 3.

With the exception of few publications, the stability constants (stepwise or overall) of UO_2^{2+} – amino acid complex species reported in the literature take account only of the following four species: $(\text{UO}_2)\text{LH}^{2+}$, $(\text{UO}_2)\text{L}_2\text{H}_2^{2+}$, $(\text{UO}_2)\text{L}^+$ and $(\text{UO}_2)\text{L}_2^0$ (with L = amino acid). Dongre *et al.* [180] reported the formation of the $(\text{UO}_2)(\alpha\text{-alanine})_4^{2-}$ species at pH = 5, Bismondo *et al.* [178] reported the formation of $(\text{UO}_2)(\text{LH})_3^{2+}$ species with L = β -alanine and γ -aminobutyric acid, at pH ≤ 3.5 . Some authors hypothesized that mixed hydroxo species can be also formed above pH 4, as shown by Gianguzza *et al.* [186] who report a high formation percentage of the $(\text{UO}_2)\text{L}(\text{OH})_2^-$

species (L = aspartate or glutamate) in the pH range (3 - 6) investigated. By including this species in their complexation model, the authors have also considered the formation of a further mixed $(\text{UO}_2)\text{L}(\text{OH})^0$ species whose formation constant was estimated considering low ligand and metal concentrations as those which can be found in natural fluids.

As a consequence of the numerous critical points that affect much of the literature stability data, it is difficult to make exhaustive consideration on the complexation capacity of this class of biological ligands under the conditions of pH, temperature, ionic strength and medium composition typical of natural fluids.

The stability of uranyl complexes is almost always the same for the α -aminoacids. The weighted average value, for the formation constant relative to the equilibrium: $\text{UO}_2^{2+} + \text{L}^- = (\text{UO}_2)\text{L}^+$, is $\log K_1(\pm 0.5) = 7.6$ ($I = 0.1 \text{ mol L}^{-1}$). Note that this value is comparable, within the fairly high confidence interval, with the sum of the single contributions calculated for the amino (5.8 ± 0.5 ; see section 3.4) and carboxylic (2.6 ± 0.2 at $I = 0.1 \text{ mol L}^{-1}$) groups: (8.4 ± 0.7 at $I = 0.1 \text{ mol L}^{-1}$).

The literature reports some data on the Gibbs free energy, enthalpy and entropy change values for the interaction of UO_2^{2+} with some aminoacids (see Table 3S of Supplementary Information). Independently of the aminoacid considered, the ΔH values of protonated complexes, involving only carboxylate in coordination, are endothermic, while they are highly exothermic for unprotonated complexes, for which amino group participates in coordination as well.

3.6. *Poly(amino carboxylates)*

The therapies used in medicine against toxic effects of uranium and other radionuclides [229] and the remediation of soils and aquatic ecosystems contaminated by toxic metal ions [230] are only a few examples of the large number of applications of poly(amino carboxylate) ligands (usually called complexones or indicated by the acronym APC) as chelating agents. They are also often used as model molecules in interpreting the chemistry of humic and fulvic acids and their reactivity towards metal ions. In this light, the knowledge of uranyl speciation in the presence of this class of ligands is of great importance and justifies the interest of researchers for the study of uranyl – APC systems. Stability data for UO_2^{2+} - complexone species are reported in many articles [100, 103, 226, 227, 231-251] and databases [40, 42]. Furthermore a critical evaluation of stability constants of species formed in metal - APC systems was reported by Anderegg et al. [252-254].

Much of the literature stability data concerns the interaction of uranyl ion with ethylenediamine-N,N,N',N'-tetraacetate (EDTA) [231, 234, 237-239, 243, 245, 248, 255], but many reports can also

be found for uranyl complexes of nitrilotriacetate (NTA), ethylene glycol-bis(2-aminoethylether)-N,N,N',N'-tetraacetate (EGTA), diethylenetriamine-N,N,N',N',N'',N''-pentaacetate (DTPA), triethylenetetraamine-N,N,N',N',N'',N''',N''''-hexaacetate (TTHA), 1,2-diaminocyclohexane-N,N,N',N'-tetracetate (DCTA), ethylenediamine-N,N'-diacetate (EDDA), Iminodiacetate (IDA) methyliminodiacetate (MIMDA) N-hydroxyethyliminodiacetate (HIMDA) N-hydroxyethyl ethylenediaminetriacetate (HEDTA) N-(2'-carboxyphenyl) iminodiacetate (HADA), and S,S'-ethylenediaminedisuccinate (S,S-EDDS) [100, 103, 217, 226, 232-235, 237, 238, 240-244, 246-249, 253]. Moreover, Hernandez *et al.* [250] reported a potentiometric study on the interaction of UO_2^{2+} ion with a new series of complexones synthesized by themselves, namely N,N,N',N'-tetrakis(carboxymethyl)-2,3-diaminopropionic acid (CEDTA), N,N,N',N'-tetrakis(carboxymethyl)-1,3-diaminobutyric acid (DBT), D,L-N,N,N',N'-tetrakis(carboxymethyl) ornithine (OTC) and N,N,N',N'-tetrakis-(carboxymethyl)lysine (LTC).

Unfortunately, even if a sufficient number of papers dealing with the binding ability of poly(amino carboxylate) compounds towards UO_2^{2+} is available, the data reported in the literature are generally not homogeneous as regards both the speciation models proposed for UO_2^{2+} – APC systems and the relative stability of complex species formed. Moreover, some of the data published do not meet criteria for critical selection by some stability constant databases (see, e.g., ref. [40]), and, therefore, will not be taken into account in this review.

Since many investigations on uranyl – APC systems were carried out in acidic pH range (usually $\text{pH} \leq 4$), only few authors reported stability data of mono- or polynuclear mixed hydrolytic $(\text{UO}_2)_p(\text{APC})_q(\text{OH})_r$ species [238, 243, 250] and only in a few cases [235, 238, 242, 243, 250] were the hydrolytic species of uranyl ion included in the speciation models proposed.

Despite the tendency of EDTA to form only mononuclear species with metal ions, almost the totality of authors reported the binuclear species $(\text{UO}_2)_2(\text{EDTA})^0$ [231, 234, 236, 237, 243, 245, 255]. In addition, Overvol *et al.* [243] reported $(\text{UO}_2)_2(\text{OH})(\text{EDTA})^+$ and $(\text{UO}_2)_2(\text{OH})_2(\text{EDTA})^{2-}$ and ascribed the formation of binuclear species to the steric hindrance by uranyl oxygen atoms that forces the EDTA to coordinate only in the equatorial sites. The same conclusion was drawn by Bhat *et al.* [231] who hypothesized that it is also caused by the weak interaction of the uranyl ion with the amino groups of the APC. Binuclear species formation of uranyl ion was also reported in the literature for TTHA $((\text{UO}_2)_2\text{LH}_2^0; (\text{UO}_2)_2\text{LH}^-, (\text{UO}_2)_2\text{L}(\text{OH})^{3-})$ [243], DTPA $((\text{UO}_2)_2\text{LH}_3^{2+}, (\text{UO}_2)_2\text{LH}^0, (\text{UO}_2)_2\text{L}^-, (\text{UO}_2)_2\text{L}(\text{OH})^{2-}$ and $(\text{UO}_2)_2\text{L}(\text{OH})_2^{3+})$ [235, 241, 243], EGTA $((\text{UO}_2)_2\text{L}^0)$ [232, 237] and HEDTA $((\text{UO}_2)_2\text{L}^+)$ [232]. Several binuclear and tetranuclear species were also found by Hernandez *et al.* [250] for CEDTA, DBT, OTC and LTC ligands.

De Stefano *et al.* [238] carried out a systematic study on the interaction of UO_2^{2+} with five APC containing different numbers of amino and carboxylic groups (TTHA, DTPA, EDTA, EGTA and NTA), in NaCl_{aq} and at $I = 0.7 \text{ mol L}^{-1}$. In the pH range investigated (2.5 – 9.5) the authors found $(\text{UO}_2)(\text{APC})\text{H}_n$ species (with $n = 0, 1, 2$ or 3). Moreover the mixed hydrolytic species $(\text{UO}_2)(\text{APC})(\text{OH})$ was found in all the systems investigated with the exception of UO_2^{2+} -TTHA. On the basis of their results, the authors also reported the following descriptive equation, valid at $I = 0.7 \text{ mol L}^{-1}$, for the dependence of the stability constant values on the number of amino, ether and carboxylic groups of the APC considered:

$$\log K(\pm 0.3) = p_1(1 + n_N) + p_2(n_{\text{-O-}} - n_{\text{COO}}) + p_3 n_{\text{COO}} n_N \quad (10)$$

where K is the equilibrium constant for the interaction of the UO_2^{2+} cation with the unprotonated or protonated poly(amino carboxylate); n_N , n_{COO} and $n_{\text{-O-}}$ are the number of amino, carboxylate and ether groups, respectively, and p_1 , p_2 and p_3 are empirical parameters. On the basis of the stability data the authors found: $p_1 = 5.8$, $p_2 = 0.78$ and $p_3 = -0.50$; the parameters are expressed with a confidence interval of 95%. This equation can be useful for the readers in calculating, with a good approximation, the formation constants of the species for other UO_2^{2+} -poly(amino carboxylate) systems.

The literature values of the stability constants of all species formed in the different UO_2^{2+} -poly(amino carboxylate) systems, together with the experimental conditions used by the different authors (ionic strength, temperature, ionic medium) and the relative thermodynamic parameters were collected in this paper (see Tables 4S and 5S of Supplementary Information).

On the basis of the stability constants values, all the authors agree with the tendency of complexones to coordinate uranyl ion by both carboxylate and amino groups [100, 226, 234, 235, 246]. Moreover, in a recent structural study, by NMR and X-ray diffraction, carried out by Palladino *et al.* [244] on the complex formation between uranyl and EDDA, the coordination of the ligand, bound to uranyl by two carboxylic and two amino groups, is confirmed in the equatorial positions.

3.7. Nucleotides

The role of metal – nucleotide complex species in biological systems (e.g. cofactor, substrate, etc.) is well documented as are the main binding sites through which nucleotides bind metal ions (phosphate groups, ring nitrogen of base and sugar hydroxyl groups). Despite the importance of metal – nucleotide complex species, a survey of the literature reveals a scarce interest towards the

interaction of uranyl with this important class of biological molecules [256-261]. Most investigations date back thirty or more years and reported only structural studies [256, 257, 259-261]. Castro *et al.* [257] reported a structural characterization of uranyl complexes formed by nucleotides 5'-AMP, ADP and ATP by ^{31}P and ^{13}C NMR spectroscopy, in the pH range 7 - 11. On the basis of NMR spectra analysis the authors asserted that the three nucleotides form different complex species with stoichiometries of $(\text{UO}_2)_2\text{L}_2$ and $(\text{UO}_2)_4\text{L}_2$. All the nucleotides bind the UO_2^{2+} ion by the ribose C-2'-OH and C-3'-OH groups. Moreover, AMP coordinates the metal ion also by the phosphate, whilst ADP and ATP bind uranyl ion through two phosphate, namely P_α , P_β and P_γ , respectively.

The only quantitative stability data on the interaction of UO_2^{2+} ion with ATP were reported by De Stefano *et al.* [258]. The authors carried out an ISE- $[\text{H}^+]$ potentiometric study both at low ionic strength (without background salt) and in NaCl or Me_4NCl at $I = 0.15 \text{ mol L}^{-1}$ at $t = 25^\circ\text{C}$. Using a suitable uranyl/ATP concentration ratio, in order to avoid the precipitation of low soluble uranium oxides in the pH range investigated (2.5 to 8.5), the authors proposed the speciation model containing the following species: $(\text{UO}_2)(\text{ATP})\text{H}_2^0$ ($\log\beta = 14.00$), $(\text{UO}_2)(\text{ATP})\text{H}^-$ ($\log\beta = 11.13$), $(\text{UO}_2)(\text{ATP})^{2-}$ ($\log\beta = 7.42$), $(\text{UO}_2)(\text{ATP})_2^{6-}$ ($\log\beta = 12.473$), $(\text{UO}_2)(\text{ATP})_2\text{H}_2^{4-}$ ($\log\beta = 21.41$) and $(\text{UO}_2)(\text{ATP})(\text{OH})^{3-}$ ($\log\beta = 0.77$). Comparison of the data obtained in the absence of ionic medium, in NaCl and in Me_4NCl allowed the authors to examine the influence of ionic medium on the stability of the complex species formed. The pH range investigated as well as the ionic strength considered and the medium used, made these thermodynamic data very interesting from the biological point of view. On the basis of the results, the authors asserted that the very stable complexes formed by uranyl with ATP in the pH range of physiological interest can seriously compromise the enzyme metabolism.

3.8. Diphosphonate complexes

Complexation of diphosphonic acids with metal ions has been a subject of study because of its importance in biological, environmental, and separation processes. One of the most widely used diphosphonic acids is 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). In particular it has found applications in sequestration of uranium after contamination and in the treatment of nuclear wastes. The investigation also extended to acid, neutral and basic range of pH, and these studies indicated several monomeric and dimeric complexes with uranyl, with different degree of protonation for HEDPA [262, 263].

Other diphosphonate ligands were reported, such as methane diphosphonic (MDPA), ethane-1,2-diphosphonic (E12DPA) and vinylidene-1,1-diphosphonic (VDPA) acids [262]. The values of stability constants are listed in Table 4. Due to the different pH range investigated (acidic or acidic/neutral/basic respectively in refs. [262, 263]), to the different ionic strength and to the quite different speciation model proposed, a comparison between the two sets of stability constants reported for HEDPA is quite difficult. The main characteristics that discriminate the two models is the presence of dimeric species [263]. It is noticeable that the formation of dimers was confirmed by the same authors [263], by electrospray ionization mass spectrometry and ^{31}P NMR. In general, the species distribution shows that with increasing pH, different species reach a high percentage of formation and that the complexation is relevant even at pH 1-2.

Moreover, ligands were reported which contain an amino group as donor, in addition to two phosphonate groups [264]. They are aminomethylenebis(phosphonic acid) (AMDP) and N,N'-dimethylaminomethylenebis(phosphonic acid) (MAMDP). The stability constants, referred to complexes formed by these two ligands are listed in Table 5. They are strong complexing agents towards uranyl, but the sequestering action becomes relevant at pH values sensibly higher if compared with HEDPA [262].

Based on the dependence of formation constants on temperature, the thermodynamic data [263] indicate that the complexation of uranyl with HEDPA is exothermic, favoured by the enthalpy of complexation. This is in contrast to the complexation of uranyl with dicarboxylic acids in which the enthalpy term usually is unfavourable.

3.9. *Mercapto complexes*

An examination of the literature concerning complexes formed by uranyl with mercapto-compounds shows that several ligands of this type have been studied, namely mercaptoethanoic acid (thioglycolic acid), 2-mercaptopropanoic acid (thiolactic acid), 3-mercaptopropanoic acid, mercaptobutanedioic acid (thiomalic acid), dimercaptobutane-dioic acid (thiotartaric acid) thiosalicylic acid, 2-amino-3-mercaptopropanoic acid (cysteine), D-2-amino-3-mercapto-3-methylbutanoic acid (penicillamine), L-5-glutamyl-L-cysteinylglycine (glutathione) [98, 179, 201, 265-273]. The formation constants are collected in Table 6. The data suggest, in particular, that only a few authors investigated these complexes with the aim of taking into account the dissociation of $-\text{SH}$ mercapto group (and, as a consequence, of studying the contribution to the stability by $-\text{S}^-$ too). Most of the authors reported the stability of complexes in which a further contribution to coordination, if any, is due to undissociated $-\text{SH}$. The involvement of $-\text{S}^-$ in coordination is

confirmed both by potentiometric evidence (dissociation of one more proton with respect to the one coming from carboxylic group) [273] and by the results obtained from IR spectra in KBr disc of uranyl mercaptopropionate complex [267]. In these spectra the band at 2577 cm^{-1} , present in the ligand alone and attributed to $-\text{SH}$, disappears in the complex. The reasons for lacking information about complex formation may be: i) the hydrolysis of uranyl ion is relevant even at acid pH values and the authors prefer to avoid the errors that become highly significant with rising pH; ii) the complexes already formed precipitate before more stable species, also involving unprotonated mercapto residues, are formed; iii) not all the mercapto ligands can form complexes with the participation of $-\text{S}^-$. Therefore we will discuss the formation constants in Table 6, by dividing them in two groups. First we consider the data determined without allowing for the dissociation of $-\text{SH}$ and the consequent coordination by $-\text{S}^-$. In this case the contribution by sulfur containing groups can only come from neutral $-\text{SH}$. As regards thioglycolic acid, there is such a dispersion of the data that the mean values of $\log\beta_{110}$ and $\log\beta_{120}$ (2.84 and 5.83) are scarcely significant, while the mean value that we can calculate from the data reported for $\log\beta_{110}$ (4.52) of thiomalic acid is fairly significant.

In previous Sections (namely: 3.1., 3.2., 3.4., 3.6.) of this review we have proposed simple equations by which, starting from the experimental values of stability constants, it is possible to roughly estimate additive single contribution for the different donor groups such as carboxylate and amino group. By employing these roughly estimated mean values, we try to estimate as well the contribution of $-\text{S}^-$ and also of $-\text{SH}$, if any. Comparing the values of $\log\beta_{110}$ determined for monocarboxylic acids of Table 6, namely thioglycolic (mean value 2.84), thiolactic (3.81), 3-mercaptopropionic (mean value 3.78) and thiosalicylic (5.01) with the value that we can estimate (which does not consider the participation of $-\text{SH}$ or $-\text{S}^-$ in coordination) for the mean stability constant of UO_2^{2+} complex with one carboxylate (2.99, eq. (5)), then, taking into account the high uncertainty referred to the above estimated value, there is probably a significant contribution to coordination only by neutral $-\text{SH}$ of thiosalicylic acid. No contribution, on the other hand, can be indicated by neutral $-\text{SH}$ of thioglycolic, while a light enhancement might be effective for thiolactic and 3-mercaptopropionic acids. The same comparison can be made for thiomalic (mean value of $\log\beta_{110} = 4.52$) and thiotartaric ($\log\beta_{110} = 3.89$) acids, with reference to a bicarboxylic ligand (the mean value estimated by eq. (5) is $\log\beta_{110} = 5.44$). Also in this case no stabilization effect due to $-\text{SH}$ can be indicated. As outlined above, some uranyl complexes listed in Table 6 were studied by considering the explicit dissociation of $-\text{SH}$ group, namely those of thioglycolic ($\log\beta_{110} = 8.17$) and thiolactic ($\log\beta_{110} = 8.87$) acids. These values of formation constants show a great stabilizing effect.

For the uranyl penicillamine complexes we found the value of $\log\beta_{110} = 12.5$ [272], obtained by the Paper Electrophoretic technique at $t = 35$ °C and $I = 0.1$ (NaClO₄). Since the arrangement of the three donor groups in the molecule is the same as in cysteine and moreover the basicity of $-\text{COO}^-$, NH_2 and $-\text{S}^-$ groups is nearly the same for these two ligands, it seems that the $\log\beta_{110}$ value, if compared with that reported for cysteine, $\log\beta_{110} = 9.04$ [200, 201, 220], should be further confirmed.

3.10. Sulfonic complexes

Another class of organic ligand, widely used in the environmental studies, and able to bind quite strongly UO_2^{2+} , is that of the sulfonic ligands. Among them, the most important is 1,2-dihydroxybenzene-3,5-disulfonic acid (Tiron), ligand which forms stable uranyl chelates over a wide pH range [274-279]. The literature reports some studies dealing with the interaction of such ligands toward uranyl, carried out at $I = 0.1$ mol L⁻¹ and $t = 20$ or 25 °C. Calculation performed on the available literature data allows one to calculate $\log\beta_{\text{pqr}}$ value for the $(\text{UO}_2)(\text{Tiron})^{2-}$, $(\text{UO}_2)(\text{Tiron})\text{H}^-$ and $(\text{UO}_2)_2(\text{Tiron})_2(\text{OH})^{5-}$ species, whose values are: 15.9, 18.8, and 28.7, respectively, at $I = 0.1$ mol L⁻¹. These data indicate the high capacity of Tiron and of sulfonic ligands in general, which are “hard” Lewis acids, to bind UO_2^{2+} . A rough comparison, between the stability constant values of the ML species of UO_2^{2+} with the different ligand classes here reported, reveals the following stability trend,

$\log\beta_{\text{ML}}$: phosphonates >> sulfonates > amines > carboxylates \geq mercapto ligands

This trend is valid only for the $(\text{UO}_2)\text{L}$ species, and can vary for the other UO_2^{2+} -ligand complexes of the speciation models; an accurate comparison of the effective sequestering ability of the different ligand classes toward UO_2^{2+} can be made only by using the procedure reported in the Section 6.

4. Humic and Fulvic acids

Humic substances (HS), being a consistent part of natural organic matter in aquatic ecosystems, play a fundamental role in the uptake/release process of metal ions by their high chelating properties due to the simultaneous presence of different binding sites (carboxylic, phenolic, amino, hydroxyl) in their structure. Despite a large number of studies on the interactions of humic (HA) and fulvic (FA) acids with uranyl [17, 141, 280-307], no critically evaluated value of stability constants for the species formed in these systems can be found in the most important compilations and databases. This lack can be attributed to the following main reasons: i) the uncertainty on the

binding sites involved in the interaction, which is strongly dependent on the pH of aqueous system under investigation, ii) the non-homogeneous structure of fulvic and humic acids which does not allow us to have a ligand unequivocally defined, and iii) the multiplicity of complexation models used by different authors to explain the coordination way of these natural macromolecules. An interesting collection and classification of the different binding models reported in the literature was done by Hummel [308], with the intention to point out the differences in calculation for the stability constants of complex species formed by “simple ligands” and by humic substances. In particular, for the latter, the author underlined the uncertainties derived from the difficulty to assess exactly i) the number and the nature of functional groups involved in metal binding, ii) the effective concentration of humic substances owing to the great variability of molecular weight, and iii) the dependence of complex species formed and their stability constants on pH and on ionic strength. Hummel [308] also reported the different attempts made by several authors to overcome these and other problems relative to the calculation of thermodynamic data by using various models, (such as the Site Complexation Capacity SCC, the Loading Capacity LC, etc.) where some parameters were considered according to the assumptions made. As a consequence, the models can be classified in: i) single site models, ii) mixed ligand models, iii) variable stoichiometry (or multidentate) models, iv) multi-site models, and v) continuous distribution models.

The stability constants of the UO_2^{2+} -HA and -FA species were calculated by authors with different models (see Tables 6S of Supplementary Information).

Czerwinski *et al.* [281] reported the stability constant of the uranyl complex with an aquatic humic acid at $\text{pH} = 4$, assuming that at this pH the hydrolysis of uranyl can be neglected. From measurements carried out by ultrafiltration, anion exchange and time resolved laser fluorescence spectroscopy (TRLFS) techniques and using a *single-site model* (namely Charge Neutralization model, CNM), the authors determined, by the loading capacity parameter (LC), the fraction of total humate concentration participating in the complexation reaction with UO_2^{2+} ion. The same complexation model was used by other authors [290, 295, 296, 298, 304] on different natural and synthetic humic acids. Despite the different experimental conditions and different humic acids used by the various authors, the stability constants obtained from these investigations, were comparable ($5.85 \leq \log\beta_{(\text{UO}_2)(\text{HS})} \leq 6.56$).

A comparison of stability constants obtained using the Charge Neutralization model (CNM) and the so-called Polyelectrolyte Model (PM) was made by Choppin *et al.* [304]. In the PM model the binding sites of humic substances are considered to be the ionized carboxylate groups and the calculated stability constant depends on the dissociation degree α of the macromolecule, and, consequently, on the pH. The difference of ~ 1 logarithm unit in the $\log\beta_{(\text{UO}_2)(\text{HS})}$ calculated at $\text{pH} =$

4, confirms that a comparison of results obtained with different models appears difficult and, in some cases impossible.

Many authors used a simple 1:1 complexation model to describe the interaction of uranyl with humate and fulvate [141, 282, 283, 285, 286, 289, 297, 306, 309]. Da Silva *et al.* [282, 283] reported a single conditional stability constant $\log K_{(\text{UO}_2)(\text{FA})}$ for different soils and anthropogenic fulvic acids at pH = 3.5 and 7. Kribek *et al.* [286] stated that, in the pH range 3.5 – 7, humic acids interact with UO_2^{2+} ion by phenolic, amino and carboxylic groups (with a greater contribution of the first two groups) and asserted that the humic acid under investigation behaves as a bidentate ligand with a conditional $\log K = 7.7$ for $(\text{UO}_2)\text{L}$ (L = HA) species. Glaus *et al.* [305, 306] used the Equilibrium Dialysis-Ligand Exchange technique (EDLE) to calculate 1:1 conditional stability constants of the UO_2 -fulvic and humic systems in the pH range 5 to 10, including the hydrolytic species of uranyl in their speciation model. The authors carried out the measurements at low $\text{UO}_2^{2+}/\text{L}$ ratios to avoid the metal saturation of binding sites of the ligands under investigation. From data reported, a consistent variation of $\log K$ results, with varying pH, from 8.24 to 13.96 for UO_2 -HA and from 7.81 to 14.49 for UO_2 -FA systems, respectively, at $I = 0.02 \text{ mol L}^{-1}$ (NaClO_4 medium).

A conspicuous number of authors used a multidentate model to study the UO_2 -HS interactions [141, 289, 291, 293, 299-301]. Shanbhang *et al.* [299] considered the humic acid as a bidentate ligand able to form 1:1 and 1:2 complex species by carboxylate sites and provides values of $\log \beta$ of 5.13 - 5.08 and 8.85 – 9.11 for the $(\text{UO}_2)(\text{HA})$ and $(\text{UO}_2)(\text{HA})_2$ species at pH = 4.04, in the temperature range 2 to 34 °C. The same model was used by Munier-Lamy *et al.* [291] for fulvic and humic acids extracted from marine sediments. The authors registered an increase of stability constants with the increasing of pH and decrease of uranyl concentration. Moreover, at low uranyl concentration, the authors report a prevalent formation of the $(\text{UO}_2)(\text{FA})_2$ and the $(\text{UO}_2)(\text{HA})$ species in the two systems, respectively.

Saito *et al.* [302, 303] applied a *multi-site model* (the so-called Multisite Ryan Weber Model, MSRW) to data on the UO_2 -HA interaction, obtained by fluorescence spectroscopy at pH = 4. The authors reported two stability constants associated with carboxylic groups with a different chemical environment ($\log K_1 = 5.07$ and $\log K_2 = 4.70$). The same model was used by Li *et al.* [288] in the study of the interaction of UO_2^{2+} with fulvic and humic acids through a combination of dialysis, ultrafiltration and fluorescence spectrometry techniques. According to the authors, both fulvic and humic acids bound uranyl by two different binding sites with different strength of interaction (two 1:1 complex species were considered in the model). The conditional stability constants of species

formed by the different binding sites differ of ~ 2 log units and fulvate forms more stable complexes than humate.

Giesy *et al.* [284] reported the stability constants of UO_2 -HA complexes obtained using two models: the Discrete multi-ligand and the Continuous multi-ligand models. The authors found that, at constant pH and ionic strength, irrespective of the model used, the stability constants of complex species formed depend on the UO_2 /HA ratio. In fact, at lower ratio (excess of HA), uranyl binds to the “more stable sites”, whilst, at higher ratio (excess of UO_2^{2+} ion) uranyl binds to all sites of humic acid. As a consequence, for the same HA concentration, the stability constant of UO_2 -HA complex species decrease with the increase of uranyl concentration in solution. This means that a single value of $\log K$ is not sufficient to describe the whole complexation behaviour of HA toward UO_2^{2+} ion. Giesy *et al.* [284] were of the opinion that, by using a continuous multi-ligand distribution model, three points (three stability constants) are needed to describe entirely the speciation of UO_2 -HA systems.

In two recent publications some further suggestions were proposed for a more accurate investigation of UO_2 -HA interactions. Pashalidis *et al.* [294] reported the formation of a mixed $(\text{UO}_2)(\text{HA})(\text{OH})$ hydrolytic species in the pH range 7.5 – 7.9. De Stefano *et al.* [307] proposed a new complexation model that can be considered a mixture of multi-ligand and multi-site models. According to this model, fulvic acid was considered to be constituted by two units, a di-carboxylic unit (FA_1) and a phenolic unit (FA_2) each playing an important role depending on the pH to be considered. Using this model, the authors proposed a speciation model with the formation of $(\text{UO}_2)(\text{FA}_1)$, $(\text{UO}_2)(\text{FA}_1)(\text{FA}_2)\text{H}$, $(\text{UO}_2)(\text{FA}_1)(\text{FA}_2)$ species in the pH range 3 to 7.

In order to facilitate the interpretation of the acid-base and complexing properties of natural organic matter, some high molecular weight polycarboxylic ligands, at different molecular weights, were used as model molecules (see Table 6S of Supplementary Information); also in this case, the experimental data were processed by using different approaches [287, 292, 307].

5. Complementary techniques

The thermodynamic stability data, which are the basis of chemical modeling of solutions containing metals and ligands that form complexes, are very often obtained by techniques such as potentiometry, UV-vis spectrophotometry or calorimetry. In recent years the evolution of new investigation techniques allows us, in some cases, to expand and fortify the speciation studies, collecting experimental data from more than one technique and providing experimental evidence for the presence of the species modelled and also some structural information on complexes in

solution. The joint elaboration of data coming from a wide range of analytical techniques and theoretical calculation often fortifies the speciation model proposed and the structural hypothesis.

EXAFS is widely utilized in order to obtain the structure of complexes in solution. This powerful technique for probing the local structure around almost any element in the periodic table (except the lightest) gives information on the number and chemical identities of near neighbours and the average interatomic distances up to 5-6 Å. The EXAFS technique can be used for atoms in any aggregation state (solid, liquid or gas) and therefore can be applied in the study aimed to modelling the solution chemistry. EXAFS spectra can be interpreted on the base of the number and type of donors and on their position with respect to the metal coordination. By combining this technique with others speciation techniques, the species hypothesised can be confirmed and their structure can be proposed. Tsushima *et al.* [310] for example, investigated the stoichiometry and structure of aqueous uranyl(VI) hydroxo dimers and trimers by spectroscopic (EXAFS, FTIR and UV-vis) and quantum chemical (DFT) methods. FTIR and UV/vis spectroscopy were used for the speciation of uranyl complexes in aqueous solution, while DFT calculations showed that $(\text{UO}_2)_2(\text{OH})_2^{2+}$ has two bridging hydroxo groups with a U-U distance of 3.875 Å, in good agreement with EXAFS, where a U-U distance of 3.88 Å was found. Rossberg *et al.* [311] studied by EXAFS the interaction of uranyl with lignin degradation products: protocatechuic acid, pyrogallol and vanillic acid. They proposed the formation, in alkaline conditions, of a five-membered ring complex with the involvement of the OH groups in *ortho* position to each other, showing that the EXAFS is useful to identify the functional groups that are involved in the metal coordination. Allen *et al.* [132] studied the interaction of uranyl with citrate, determining the structure of the different complexes formed.

Mass spectrometry is another analytical technique that can be useful to confirm the presence of complex species in solution. In particular the ESI-MS (Electrospray ionisation Mass Spectrometry), that allows the direct introduction of solutions in the ionization system, proved to be useful for stoichiometry identification of complexes. Examples of applications on uranyl speciation are the works of Jacopin *et al.* [312] and Reed *et al.* [263] who studied the complexation between uranyl(VI) and 1-hydroxyethane-1,1-diphosphonic acid. The ESI-MS data confirm the stoichiometry of complexes in solution, proposed on the basis of potentiometric and spectroscopic techniques (1:1, 1:2, and 2:2 complexes) and recognize the presence of uranyl-HEDPA cluster complexes containing H_2O and HClO_4 .

Another example of ESI-MS application is the investigation of uranyl-citrate system proposed by Pasilis and Pemberton [149] and Somogyi *et al.* [313]. In this case the researchers clarify the equilibria distribution of uranyl-citrate complexes and presented evidence for three structurally

distinct uranyl-citrate complexes $[(\text{UO}_2)_2(\text{cit})_2]^{2-}$, $(\text{UO}_2)_3(\text{cit})_2$ and $(\text{UO}_2)_3(\text{cit})_3^{3-}$ which exist in dynamic equilibrium over a pH range consistent with environmental conditions.

Several spectroscopic techniques can be applied to investigate solution speciation and with most of them it is possible to obtain data useful for the formulation of speciation models and for the calculation of species formation constants. Each of these techniques can also often provide complementary information on the coordination mode and/or on the structure of complexes. The application of ^1H and ^{13}C NMR metal-ligand solutions, for example, provides $^{13}\text{C} - ^1\text{H}$ coupling constants that are good indicators for metal-ligand binding [314] because the coupling constants of nuclei closer to a metal binding site will be significantly different than those in the free ligand, and the J_{CH} difference diminishes for nuclei further from the metal binding site. A recent application of this technique is, for example, the work of Xie *et al.* [315] who studied the complexes of uranyl with histidine, N-acetyl-histidine, tyrosine, and N-acetyl-tyrosine by potentiometry, UV-visible and NMR spectroscopy. The authors proposed a chemical model for uranyl-aminoacid solutions based on the potentiometric data and, on the NMR data. They hypothesize that the imidazole ring is not participating in an inner-sphere interaction with uranyl. Analogous information can be taken from IR spectrometry. The position, the broadening and the intensity of IR bands provide information on the ligand functional groups involved in the metal coordination. Nevertheless, the classical application of IR technique needs the manipulation of aqueous samples and may perturb the equilibrium conditions; moreover, the structural information, obtained from spectra recorded with solid KBr pellet, may not be coherent with structures of complexes in aqueous solution [316]. The application of the Attenuated Total Reflection (ATR) Fourier Transform Infrared (FTIR) spectroscopy overcomes this difficulty because it is directly applicable to liquid samples. An example of application of ATR-FTIR is the recent work of Barkleit *et al.* [316]. They present spectroscopic results on the complexation of uranyl with L-phenylalanine and with the homologous ligand phenylpropionate missing the amino functional group in aqueous solution. The results provide a description of the binding states of the uranyl complexes in aqueous solution at pH 3.2. A bidentate binding of the carboxylate group to the uranyl ion was observed by the characteristic shifts of the carboxylate modes and the contributions of the amino group to the binding to the uranyl ion in the amino acid complex can be ruled out.

Fluorescence spectroscopy is another spectroscopic technique widely utilized for uranyl chemistry investigations because the characteristic fluorescence of uranyl ion. In particular, the application of Time Resolved Laser Induced Fluorescence Spectroscopy, which can record the fluorescent spectra and determine fluorescence lifetimes, is very useful in investigating uranyl behaviour. The application of TRLFS allows one to obtain, as with potentiometry or UV-vis spectrophotometry, a

speciation model and the complexation constants. However it has the disadvantage of possible quenching phenomena due to reactions with natural organic substances or radiationless decay via non-fluorescent parasitical metal ions, e.g., Fe^{3+} and radical formation, e.g., by carbonate ions [154, 155]. Notwithstanding this, the TRLFS has the advantage that is applicable to solutions with very low concentration, therefore could be useful for speciation studies where the uranyl concentration is comparable with the environmental levels. Example of recent applications of this technique are the work of Moll *et al.* [155] and Feldman *et al.* [133], where TRLFS was used to study the uranyl speciation with α -substituted carboxylic acids and citrate, respectively. The authors hypothesised a model speciation and calculate complexation constant values from fluorescence data recorded on 10^{-5} M uranyl solutions. The analytical techniques that are usually utilized for speciation studies and respect the equilibrium condition cannot be applied at this low concentration levels.

6. Sequestering ability of different ligand classes

Comparison of the yield of formation of different metal-ligand systems depends on factors, such as concentrations and concentration ratios of reactants and pH, and on the acid-base properties of the metal (hydrolysis) and the ligand (protonation), since both the hydrolysis and the protonation reaction are competitive with respect to the metal complex formation reaction. Owing to different acid-base properties, two metal-ligand systems may show the same formation percentages (at a given pH value), even with different formation constants, or viceversa. Moreover, weak interactions with the supporting electrolyte may also alter the comparison. In fact the anion of the supporting electrolyte may form weak species with the metal cation (see also section 2) and the ligands can interact with the cation (e.g. carboxylates) or the anion (e.g. protonated amines) [114, 161, 162, 317, 318]. To overcome the difficulty of taking simultaneously into account these factors the use of a sigmoid Boltzmann-type equation was proposed [107, 160]

$$x = \frac{1}{1 + 10^{(pL - pL_{0.5})}} \quad (11)$$

where x is the fraction of the metal M complexed by the ligand. The parameter $pL_{0.5}$, calculated by least squares analysis, gives the conditions for which 50% of metal is complexed by the ligand ($[\text{L}]_{\text{tot}} = 10^{-pL_{0.5}}$). Other details on the sequestering capacity expressed by eq (11) are reported in ref. [319]. Several examples for the sequestering capacity of different ligands towards uranyl were reported in a recent article [107, 160]. In Figure 3, we show the plot of x (molar fraction) vs. pL for

the sequestration of uranyl by citrate, AMDP, polyallylamine, Tiron, DTPA and HEDPA, whose $pL_{0.5}$ value is: 6.7, 7.1, 5.4, 5.7, 5.1 and 4.9, respectively at $t = 25\text{ }^{\circ}\text{C}$ and $I = 0.1\text{ mol L}^{-1}$.

This diagram reflects very well the sequestering ability of the ligands taken into account. Moreover, calculations of $pL_{0.5}$ can be made under different conditions of ionic strength, ionic medium, pH and temperature. The comparison of the sequestering abilities of citrate and Tiron shows how the value of pH can invert the trend of $pL_{0.5}$. In fact, at $\text{pH} = 5$, cit ($pL_{0.5} = 6.7$) > Tiron ($pL_{0.5} = 5.7$), whilst at $\text{pH} = 8$ we have Tiron ($pL_{0.5} = 8.4$) >> cit ($pL_{0.5} = 5.8$). Other significant examples are given in the articles reporting values of $pL_{0.5}$ in different conditions [107, 109, 110, 160, 172, 238].

7. Final remarks

The great interest of the scientist community for equilibrium studies involving uranium(VI) chemistry in solution, with the aim of improving the knowledge of uranium(VI) speciation, is shown by the large number of papers published on this topic. Among the several reports, appearing in the last decade, most deal with this topic by extending investigation to wide ranges of ionic strength and temperature and by considering complementary techniques which, in addition to the classical potentiometry and UV-Vis spectrophotometry, can improve and complete the information about speciation and structure of complexes. In other words, much reliable analytical data is now available to assess the speciation of uranium(VI) in natural waters and biological fluids.

In general, the stability of uranyl complexes we reviewed can be correlated with the nature and the number of donor groups in the ligand molecule. In some cases, if the number and the homogeneity of literature data allowed us, we have proposed empirical equations, useful to estimate the values of stability constants only as a function of the stoichiometry of the complex, the nature of donor groups and also of ionic strength. The elaboration of all the carboxylate ligand stability constant data allows us to propose an expression (eq. (5)), that takes into account only the number of carboxylic groups, by which it is possible to estimate the formation constants with a mean error ($\epsilon(\log K)$) of ± 0.3 . With the same equation we can estimate the formation constant for an uranyl complex not directly studied. Similar relationships were found as well for complexes formed by ligands containing only amino donor groups. Among the different ligand classes taken into account, we must emphasize the role of the diphosphonate ligands, which not only can form very stable species, but can do so in a quite acidic pH range (this feature distinguishes these ligands from any other one in this context).

Regarding the application of these data in building chemical speciation models, the data suggest some considerations: i) for some ligands (as an example, hydroxyl, citrate, oxalate) the data

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reported are exhaustive; ii) for other ligands, not less relevant, the information should be improved by extending investigation to variable temperature, ionic strength and ionic medium; iii) for some ligands (as an example, mercapto and sulfonic ligands), the information is quite lacking.

Finally, always with the aim of suggesting applications to solve speciation problems, the sequestering ability of the different ligands has been evaluated by applying eq.(11). In such a way direct information can be obtained about the complexing capability of a ligand, by taking into account the actual experimental conditions of the solution under examination, as described in Section 6.

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Table 1. Hydrolytic constants of UO_2^{2+} and corresponding enthalpies at infinite dilution and $t = 25\text{ }^\circ\text{C}$

$(\text{UO}_2)(\text{OH})^+$	$(\text{UO}_2)_2(\text{OH})_2^{2+}$	$(\text{UO}_2)_3(\text{OH})_5^+$	$(\text{UO}_2)_3(\text{OH})_4^{2+}$	$(\text{UO}_2)_2(\text{OH})_3^+$	$(\text{UO}_2)(\text{OH})_2$	$(\text{UO}_2)(\text{OH})_3^-$	$(\text{UO}_2)(\text{OH})_4^{2-}$	$(\text{UO}_2)_3(\text{OH})_7^-$	$(\text{UO}_2)_4(\text{OH})_7^+$	Ref.
$\log\beta_{\text{pq}}^\circ$										
-5.8±0.2 ^{a)}	-5.62±0.04	-15.63±0.08	-11.75±0.10	-	-	-	-	-	-	[43]
-5.9±0.1	-5.58±0.04	-16.0	-	-	-	-	-	-	-	[45]
-5.2±0.3	-5.62±0.04	-15.55±0.12	-11.90±0.3	-2.7±1.0	~-10.3	-19.2±0.4	-33±2	-31±2	-21.9±1.0	[44]
-5.25±0.24	-5.62	-15.55	-11.9	-2.7	-12.15±0.07	-	-32.4±0.7	-32.2±0.8	-21.9	[39]
-5.1±0.1	-5.56±0.6	-15.46±0.09	-11.7±0.2	-	-	-	-	-	-22.1±0.2	[50]
-5.19±0.05	-5.76±0.04	-15.89±0.06	-11.82±0.08	-	-	-	-	-29.26±0.10	-	[47]
-5.58±0.24	-5.83±0.02	-16.37±0.02	-	-	-	-	-	-	-	[51]
$\Delta H/\text{kJmol}^{-1}$										
44	41.8	108	-	-	-	-	-	-	-	[45]
40.7±2.9	47.8±1.3	119.5±2.0	98.9±0.5	-	-	-	-	177±7	-	[53]
46.5±3.7	48.2±1.7	120.1±1.6	-	-	-	-	-	-	-	[51]

^{a)} 95% of confidence interval

Table 2. Suggested thermodynamic values for the hydrolysis of UO_2^{2+} at infinite dilution and $t = 25$ °C, calculated in this work

p	q	$\log\beta_{pq}^\circ$	ΔG° ^{a)}	ΔH° ^{a)}	$T\Delta S^\circ$ ^{a)}
1	1	-5.8 ± 0.15 ^{b)}	33.1 ± 0.9	42 ± 4	9 ± 4.0
2	2	-5.62 ± 0.05	32.1 ± 0.3	48.1 ± 1.1	16 ± 1.1
3	5	-15.61 ± 0.1	89.1 ± 0.6	120 ± 1.1	30.9 ± 1.2
3	4	-11.82 ± 0.08	67.5 ± 0.5	99 ± 3.0	32 ± 3.0
2	1	-2.9 ± 0.3	16.6 ± 1.7	22 ± 8.0	5 ± 8.0
1	2	-11.1 ± 0.6	63 ± 3.0	72 ± 8.0	9 ± 9.0
1	3	-19.7 ± 0.6	112 ± 3.0	101 ± 10	-11 ± 11
1	4	-32.7 ± 0.5	187 ± 3.0	131 ± 10	-56 ± 10
3	7	-31 ± 0.8	177 ± 5.0	180 ± 8.0	3 ± 9.0
4	7	-22 ± 0.8	126 ± 5.0	160 ± 10	34 ± 11

^{a)} kJ mol^{-1} ; ^{b)} 95% of confidence interval

Table 3. Values of $\log K^\circ$ and $\log \beta^\circ$ for the equilibrium reactions indicated, at $t = 25\text{ }^\circ\text{C}$ and $I = 0\text{ mol L}^{-1}$ [39], for carbonate and phosphate complexes.

Type of reaction	
Carbonate	$\log \beta^\circ$
$\text{UO}_2^{2+} + \text{CO}_3^{2-} = (\text{UO}_2)(\text{CO}_3)^0$	9.94
$\text{UO}_2^{2+} + 2 \text{CO}_3^{2-} = (\text{UO}_2)(\text{CO}_3)_2^{2-}$	16.61
$\text{UO}_2^{2+} + 3 \text{CO}_3^{2-} = (\text{UO}_2)(\text{CO}_3)_3^{4-}$	21.84
Phosphate	$\log K^\circ$
$\text{UO}_2^{2+} + \text{PO}_4^{3-} = (\text{UO}_2)(\text{PO}_4)^-$	13.25
$\text{UO}_2^{2+} + \text{HPO}_4^{2-} = (\text{UO}_2)(\text{HPO}_4)^0$	7.24 ^{a)}
$\text{UO}_2^{2+} + \text{H}_3\text{PO}_4 = (\text{UO}_2)(\text{H}_2\text{PO}_4)^+ + \text{H}^+$	1.12
$\text{UO}_2^{2+} + 2 \text{H}_3\text{PO}_4 = (\text{UO}_2)(\text{H}_2\text{PO}_4)_2^0 + 2 \text{H}^+$	0.64

^{a)} For equilibrium reaction $\text{UO}_2^{2+} + \text{HPO}_4^{2-} = (\text{UO}_2)(\text{HPO}_4)^0$ the values of $\log K^\circ = 7.18$ and 7.28 were also reported, from spectroscopic measurements and solubility experiments, respectively [39].

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Table 4. Values of $\log\beta_{pqr}$ for uranyl complexes with HEDPA (H_4L), at $t = 25\text{ }^\circ\text{C}$ and $I = 1.0\text{ M }(\text{CH}_3)_4\text{NCl}^{\text{a}}$ or $I = 0.1\text{ M }(\text{CH}_3)_4\text{NCl}^{\text{b}}$

Reaction	pqr	$\log\beta_{pqr}$	$\log\beta_{pqr}$	$\log\beta_{pqr}$	$\log\beta_{pqr}$
		HEDPA	MDPA ^{b)}	VDPA ^{b)}	E12DPA ^{b)}
$\text{UO}_2^{2+} + \text{L}^{4-} + 2\text{H}^+ = (\text{UO}_2)\text{LH}_2^0$					20.81
$\text{UO}_2^{2+} + \text{L}^{4-} + 3\text{H}^+ = (\text{UO}_2)\text{LH}_3^+$	113	24.43 ^{a)} 25.31 ^{b)}	24.72	24.35	
$\text{UO}_2^{2+} + 2\text{L}^{4-} + 4\text{H}^+ = (\text{UO}_2)\text{L}_2\text{H}_4^{2-}$	124	44.90 ^{a)} 49.17 ^{b)}	48.20	47.24	
$\text{UO}_2^{2+} + 2\text{L}^{4-} + 3\text{H}^+ = (\text{UO}_2)\text{L}_2\text{H}_3^{3-}$	123	41.00 ^{a)}			
$\text{UO}_2^{2+} + 2\text{L}^{4-} + 2\text{H}^+ = (\text{UO}_2)\text{L}_2\text{H}_2^{4-}$	122	35.94 ^{a)} 46.40 ^{b)}	45.47	44.69	39.25
$\text{UO}_2^{2+} + 2\text{L}^{4-} + \text{H}^+ = (\text{UO}_2)\text{L}_2\text{H}^{5-}$	121	28.87 ^{a)}			
$\text{UO}_2^{2+} + 2\text{L}^{4-} = (\text{UO}_2)\text{L}_2^{6-}$	120	18.93 ^{a)}			
$\text{UO}_2^{2+} + 2\text{L}^{4-} + \text{H}_2\text{O} = (\text{UO}_2)\text{L}_2(\text{OH})^{3-}$	12-1	7.17 ^{a)}			
$2\text{UO}_2^{2+} + 2\text{L}^{4-} + \text{H}^+ = (\text{UO}_2)_2\text{L}_2\text{H}^{3-}$	221	33.70 ^{a)}			
$2\text{UO}_2^{2+} + 2\text{L}^{4-} = 2(\text{UO}_2)_2\text{L}_2^{4-}$	220	24.03 ^{a)}			
$2\text{UO}_2^{2+} + 2\text{L}^{4-} + \text{H}_2\text{O} = (\text{UO}_2)_2\text{L}_2(\text{OH})^{5-}$	22-1	12.92 ^{a)}			

^{a)} Ref. [263]; the protonation constants are: for HEDPA: $\log K_1^H = 11.36$, $\log K_2^H = 6.89$, $\log K_3^H = 2.63$, $\log K_4^H = 1.45$.

^{b)} Ref. [262], the protonation constants are: for HEDPA: $\log K_1^H = 10.52$, $\log K_2^H = 6.80$, $\log K_3^H = 2.50$, $\log K_4^H = 1.49$; for MDPA: $\log K_1^H = 10.05$, $\log K_2^H = 6.85$, $\log K_3^H = 2.60$, $\log K_4^H = 1.51$; for VDPA: $\log K_1^H = 10.04$, $\log K_2^H = 6.67$, $\log K_3^H = 2.41$, $\log K_4^H = 1.47$; for E12DPA: $\log K_1^H = 8.53 \pm$, $\log K_2^H = 6.94$, $\log K_3^H = 2.46$, $\log K_4^H = 1.25$.

Table 5. Values of $\log\beta_{pqr}$ for uranyl complexes with AMDP and MAMDP (H_4L), at $t = 25\text{ }^\circ\text{C}$ and $I = 0.1\text{ (CH}_3)_4\text{NCl}$ ^{a)}

Reaction	pqr	$\log\beta_{pqr}$	
		AMDP	MAMDP
$UO_2^{2+} + L^{4-} = (UO_2)L^{2-}$	110	25.9	24.8
$UO_2^{2+} + L^{4-} = (UO_2)L(OH)^{3-}$	11-1	15.5	14.1
$UO_2^{2+} + L^{4-} = (UO_2)L(OH)_2^{4-}$	11-2	4.2	2.1
$UO_2^{2+} + L^{4-} + H^+ = (UO_2)LH^+$	111	32.6	34.6
$UO_2^{2+} + L^{4-} + 2H^+ = (UO_2)LH_2^\circ$	112	38.6	39.9
$UO_2^{2+} + 2L^{4-} = (UO_2)L_2^{6-}$	120	30.5	32.4
$UO_2^{2+} + 2L^{4-} + H^+ = (UO_2)L_2H^{5-}$	121	41.5	-
$UO_2^{2+} + 2L^{4-} + 2H^+ = (UO_2)L_2H_2^4$	122	51.8	54.2
$UO_2^{2+} + 2L^{4-} + 3H^+ = (UO_2)L_2H_3^{3-}$	123	58.4	61.6
$UO_2^{2+} + 2L^{4-} + 4H^+ = (UO_2)L_2H_4^{2-}$	124	63.4	66.6

^{a)} Ref. [264], the values of protonation constants are for AMDP : $\log K_1^H = 11.72$, $\log K_2^H = 8.42$, $\log K_3^H = 5.42$, $\log K_4^H = 1.4$; for MAMDP: $\log K_1^H = 13.4$, $\log K_2^H = 9.18$, $\log K_3^H = 5.01$, $\log K_4^H = 1.3$.

Table 6. Stability constants values for some uranyl-mercapto compound complexes, extrapolated to zero ionic strength [161, 162]

Ligand	t / °C	$\log\beta_{110}$	$\log\beta_{120}$	$\log\beta_{130}$	ref.
Thioglycolic acid	30	3.29	5.90	-	[179]
	30	2.83	6.37		[268]
	31	2.93	5.11		[270]
	25	2.30	3.83	5.13	[265]
	25	8.17 ^{a)}	14.75 ^{a)}		[266]
Thiolactic acid		3.81	7.56		[267]
Thiolactic acid	30	8.87 ^{a),b)}	16.24 ^{a),b)}		[273]
3-mercaptopropionic acid	30	3.66			[201]
	31	3.90			[270]
Thiomalic acid	31	4.65			[269]
	30	4.39	7.70		[179]
	30	4.53	7.18		[98]
	30	4.53			[271]
Thiotartaric acid	30	3.89	6.29		[98]
Thiosalicylic acid	30	5.01	9.13		[201]

^{a)} Values obtained by considering also the dissociation of –SH group; ^{b)} ionic strength not stated

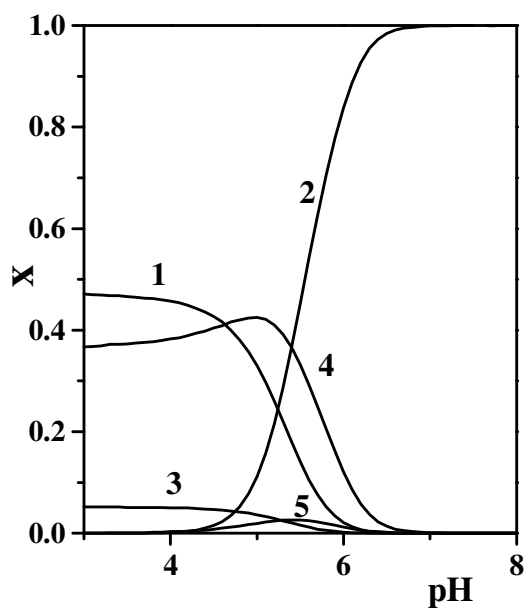


Fig. 1. Distribution of UO_2^{2+} -inorganic species at $t = 25\text{ }^\circ\text{C}$ in Synthetic Sea Water at Salinity 35‰. Component concentration (mol L^{-1}) of the SSWE at 35 ‰: $\text{Na}^+ = 0.4797$; $\text{Ca}^{2+} = 0.0111$; $\text{Mg}^{2+} = 0.0548$; $\text{F}^- = 7 \cdot 10^{-5}$; $\text{Cl}^- = 0.5650$; $\text{SO}_4^{2-} = 0.0288$; $\text{CO}_3^{2-} = 0.002$. metal: $\text{UO}_2^{2+} = 1 \cdot 10^{-7} \text{ mol L}^{-1}$.

The indexes (X) refer to the sum of the percentages of the uranyl-inorganic species: 1. $\sum \text{UO}_2^{2+}$ -fluoride species; 2. $\sum \text{UO}_2^{2+}$ -carbonate species; 3. $\sum \text{UO}_2^{2+}$ -chloride species; 4. $\sum \text{UO}_2^{2+}$ -sulfate species; 5. $\sum \text{UO}_2^{2+}$ -hydroxide species. This diagram was drawn by using the stability constants reported in Tables 2 and 3.

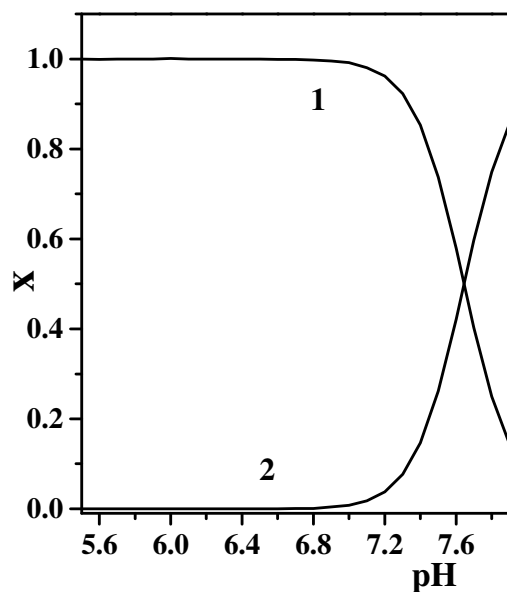


Fig. 2. Distribution of UO_2^{2+} -inorganic species at $t = 25\text{ }^\circ\text{C}$ in Synthetic Sea Water at Salinity 35‰ in presence of phosphate.

Component concentration (mol L^{-1}) of the SSWE at 35 ‰: $\text{Na}^+ = 0.4797$; $\text{Ca}^{2+} = 0.0111$; $\text{Mg}^{2+} = 0.0548$; $\text{F}^- = 7 \cdot 10^{-5}$; $\text{Cl}^- = 0.5650$; $\text{SO}_4^{2-} = 0.02880$; $\text{CO}_3^{2-} = 0.002$. metal: $\text{UO}_2^{2+} = 1 \cdot 10^{-7} \text{ mol L}^{-1}$; $\text{PO}_4^{3-} = 5 \cdot 10^{-5} \text{ mol L}^{-1}$.

The indexes (X) refer to the sum of the percentages of the uranyl-inorganic species: 1. $\sum \text{UO}_2^{2+}$ -phosphate species; 2. $\sum \text{UO}_2^{2+}$ -carbonate species. This diagram was drawn by using the stability constants reported in Tables 2 and 3.

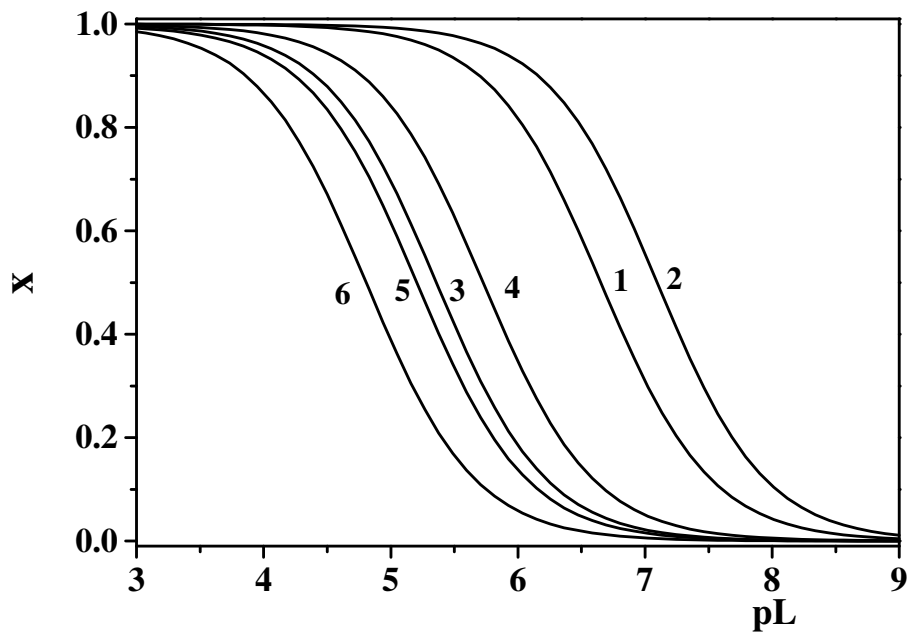


Fig. 3 Sequestration diagram of some UO_2^{2+} -ligand systems at $t = 25\text{ }^\circ\text{C}$, $I = 0.1\text{ mol L}^{-1}$ and $\text{pH} = 5$. $C_{\text{UO}_2^{2+}} = 1 \cdot 10^{-9}\text{ mol L}^{-1}$. The index (X) refers to the sum of the percentages of the uranyl-ligand species. Index: 1. cit; 2. AMDP; 3. paam; 4. Tiron; 5. DTPA; 6. HEDPA

Table 1S Literature values of the uranyl-carboxylate stability constant complexes

Ligand	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	medium	UO_2^{2+}	L	H^+/OH^-	$\log\beta_{\text{pqr}}$	Ref.
acetate	0.3	25	NaCl	1	1	0	2.6	[82]
	1	25	NaCl	1	1	0	2.32	
	2	25	NaCl	1	1	0	2.52	
	3	25	NaCl	1	1	0	2.84	
	4	25	NaCl	1	1	0	3.09	
	5	25	NaCl	1	1	0	3.14	
	2	25	NaCl	1	2	0	5.12	
	3	25	NaCl	1	2	0	5.25	
	4	25	NaCl	1	2	0	5.72	
	0	25	NaCl	1	1	0	2.86	[108]
	0.119	25	NaCl	1	1	0	2.44	
	0.504	25	NaCl	1	1	0	2.38	
	0.734	25	NaCl	1	1	0	2.36	
	0.975	25	NaCl	1	1	0	2.33	
	0	25	NaCl	1	2	0	4.62	
	0.119	25	NaCl	1	2	0	4.02	
	0.504	25	NaCl	1	2	0	4.09	
	0.734	25	NaCl	1	2	0	4.02	
	0.975	25	NaCl	1	2	0	4.24	
	0	25	NaCl	1	3	0	7.22	
	0.119	25	NaCl	1	3	0	6.58	
	0.504	25	NaCl	1	3	0	6.44	
	0.734	25	NaCl	1	3	0	6.43	
	0.975	25	NaCl	1	3	0	6.4	
	0	25	NaCl	1	3	-1	2.14	

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0.119	25	NaCl	1	3	-1	1.92	
0.504	25	NaCl	1	3	-1	1.79	
0.734	25	NaCl	1	3	-1	1.77	
0.975	25	NaCl	1	3	-1	1.78	
1	25	NaClO ₄	1	1	0	2.58	[90]
1	20	NaClO ₄	1	1	0	2.38	[101]
1	25	NaClO ₄	1	1	0	2.42	[91]
0.1	25	NaClO ₄	1	1	0	2.6	[81]
1	20	NaClO ₄	1	1	0	2.4	[92]
0.1	25	NaClO ₄	1	1	0	2.6	[61]
1	25	NaClO ₄	1	1	0	2.46	[93]
0.16	25	KNO ₃	1	1	0	2.38	
2	25	NaNO ₃	1	1	0	2.72	[80]
2	25	NaNO ₃	1	1	0	2.67	[90]
1	25	NaClO ₄	1	2	0	4.37	[101]
1	20	NaClO ₄	1	2	0	4.36	[91]
1	25	NaClO ₄	1	2	0	4.41	[92]
1	20	NaClO ₄	1	2	0	4.42	[61]
0.1	25	NaClO ₄	1	2	0	4.9	[83]
1	25	NaClO ₄	1	2	0	4.38	[101]
1	25	NaClO ₄	1	3	0	6.86	[93]
1	20	NaClO ₄	1	3	0	6.34	[101]
0.16	25	KNO ₃	1	3	0	6.38	[92]
1	25	NaClO ₄	1	3	0	6.4	[61]
1	20	NaClO ₄	1	3	0	6.37	[83]
0.1	25	NaClO ₄	1	3	0	6.3	[61]
1	25	NaClO ₄	1	3	0	6.52	[83]

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	0.1	25	NaClO ₄	1	1	0	4.62	[113]
malonate	0	25	NaCl	1	1	0	6.569	[106]
	0.1	25	NaCl	1	1	0	5.713	
	0.25	25	NaCl	1	1	0	5,452	
	0.5	25	NaCl	1	1	0	5,267	
	0.75	25	NaCl	1	1	0	5,179	
	1	25	NaCl	1	1	0	5.133	
	0	25	NaCl	1	2	0	10.551	
	0.1	25	NaCl	1	2	0	9.661	
	0.25	25	NaCl	1	2	0	9.348	
	0.5	25	NaCl	1	2	0	9.076	
	0.75	25	NaCl	1	2	0	8.902	
	1	25	NaCl	1	2	0	8.769	
	0	25	NaCl	2	2	-2	4.36	
	0.1	25	NaCl	2	2	-2	3.183	
	0.25	25	NaCl	2	2	-2	2.701	
	0.5	25	NaCl	2	2	-2	2.21	
	0.75	25	NaCl	2	2	-2	1.841	
	1	25	NaCl	2	2	-2	1.524	
	0.1	25	KNO ₃	1	1	0	5.98	
	0.1	25	KNO ₃	1	2	0	10.08	
	0.1	25	KNO ₃	2	2	-2	4.5	
	0.1	25	KNO ₃	2	2	-1	9.23	
	0.1	30	NaClO ₄	1	1	0	5.56	[98]
	1	25	NaClO ₄	1	1	0	5.42	[86]
	0.1	31	NaClO ₄	1	1	0	5.2	[89]
	0.5	25	KNO ₃	1	1	0	5.66	[94]

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	0.2	30	NaClO ₄	1	1	0	4.88	[84]
	1	25	KNO ₃	1	1	0	5.66	[87]
	0	30	NaCl	1	1	0	6.2	[95]
	0.1	31	NaClO ₄	1	1	0	5.28	[96]
	0.1	30	NaClO ₄	1	2	0	9.36	[98]
	1	25	NaClO ₄	1	2	0	9.48	[86]
	0.1	31	NaClO ₄	1	2	0	9.21	[89]
	0.5	25	KNO ₃	1	2	0	9.66	[94]
	0.2	30	NaClO ₄	1	2	0	8.63	[84]
	1	25	KNO ₃	1	2	0	9.66	[87]
	0	30	NaCl	1	2	0	9.46	[95]
	0.1	31	NaClO ₄	1	2	0	9.29	[96]
succinate	0	25	NaCl	1	1	0	5.091	[106]
	0.1	25	NaCl	1	1	0	4.249	
	0.25	25	NaCl	1	1	0	4.007	
	0.5	25	NaCl	1	1	0	3.854	
	0.75	25	NaCl	1	1	0	3.798	
	1	25	NaCl	1	1	0	3.784	
	0	25	NaCl	1	2	0	7.61	
	0.1	25	NaCl	1	2	0	6.748	
	0.25	25	NaCl	1	2	0	6.479	
	0.5	25	NaCl	1	2	0	6.28	
	0.75	25	NaCl	1	2	0	6.179	
	1	25	NaCl	1	2	0	6.12	
	0	25	NaCl	1	2	1	11.98	
	0.1	25	NaCl	1	2	1	10.77	
	0.25	25	NaCl	1	2	1	10.481	

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	0.5	25	NaCl	1	2	1	10.375	
	0.75	25	NaCl	1	2	1	10.415	
	1	25	NaCl	1	2	1	10.517	
	0	25	NaCl	2	2	-2	2.38	
	0.1	25	NaCl	2	2	-2	1.398	
	0.25	25	NaCl	2	2	-2	1.2	
	0.5	25	NaCl	2	2	-2	1.182	
	0.75	25	NaCl	2	2	-2	1.287	
	1	25	NaCl	2	2	-2	1.444	
	0.1	25	KNO ₃	1	1	0	4.29	
	0.1	25	KNO ₃	1	2	0	6.7	
	0.1	25	KNO ₃	1	1	1	7.58	
	0.1	30	NaClO ₄	1	1	0	4.48	[98]
	0.5	25	KNO ₃	1	1	0	3.87	[94]
	1	25	KNO ₃	1	1	0	3.68	[80]
	1	25	NaCl	1	1	0	3.85	[85]
	1	20	NaClO ₄	1	1	0	2.53	[92]
	0.1	31	NaClO ₄	1	1	0	4.22	[88]
	1	25	KNO ₃	1	1	0	3.68	[87]
	0.1	30	NaClO ₄	1	2	0	7.78	[98]
	1	25	NaCl	1	2	0	7.41	[85]
	1	25	NaCl	1	2	1	11.28	
azelate	0	25	NaCl	1	1	0	4.27	[106]
	0.1	25	NaCl	1	1	0	3.44	
	0.25	25	NaCl	1	1	0	3.222	
	0.5	25	NaCl	1	1	0	3.109	
	0.75	25	NaCl	1	1	0	3.093	

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	1	25	NaCl	1	1	0	3.119	
	0	25	NaCl	1	1	1	8.641	
	0.1	25	NaCl	1	1	1	7.825	
	0.25	25	NaCl	1	1	1	7.624	
	0.5	25	NaCl	1	1	1	7.538	
	0.75	25	NaCl	1	1	1	7.55	
	1	25	NaCl	1	1	1	7.603	
	0	25	NaCl	1	2	0	7.78	
	0.1	25	NaCl	1	2	0	6.964	
	0.25	25	NaCl	1	2	0	6.762	
	0.5	25	NaCl	1	2	0	6.676	
	0.75	25	NaCl	1	2	0	6.688	
	1	25	NaCl	1	2	0	6.742	
	0	25	NaCl	2	2	0	12	
	0.1	25	NaCl	2	2	0	10.36	
	0.25	25	NaCl	2	2	0	9.94	
	0.5	25	NaCl	2	2	0	9.741	
	0.75	25	NaCl	2	2	0	9.737	
	1	25	NaCl	2	2	0	9.817	
	0	25	NaCl	2	1	-2	-1.43	
	0.1	25	NaCl	2	1	-2	-2.481	
	0.25	25	NaCl	2	1	-2	-2.775	
	0.5	25	NaCl	2	1	-2	-2.951	
	0.75	25	NaCl	2	1	-2	-3.005	
	1	25	NaCl	2	1	-2	-3.007	
	0.1	25	KNO ₃	1	1	0	5.88	[97]
oxalate	1	25	NaCl	1	1	0	5.87	[127]

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1	25	NaCl	1	2	0	10.484	
1	25	NaCl	1	3	0	12.61	
1	25	NaCl	1	1	-1	0.62	
1	25	NaCl	1	1	-2	-6,25	
1	25	NaCl	1	2	-1	3,93	
1	25	NaCl	1	3	-1	5,32	
1	25	NaCl	1	3	1	16,02	
1	25	NaCl	2	5	0	25,55	
0	25	NaCl	1	1	0	7.05	
0	25	NaCl	1	2	0	11.45	
0	25	NaCl	1	3	0	11.92	
0	25	NaCl	1	1	-1	1.03	
0	25	NaCl	1	1	-2	-6.9	
0	25	NaCl	1	2	-1	3.41	
0	25	NaCl	1	3	-1	4.1	
0	25	NaCl	1	3	1	17.08	
0	25	NaCl	2	5	0	24.98	
1	25	NaClO ₄	1	1	0	6.02	[128]
3	25	NaClO ₄	1	1	0	6.39	
3	25	NaClO ₄	1	1	0	6.31	[118]
0	25	NaCl	1	1	0	7.41	
0.1	20	NaClO ₄	1	1	0	4.63	[92]
0.1	20	NaClO ₄	1	1	0	6.36	[123]
1	20	NaClO ₄	1	1	0	5.99	
1	25	NaClO ₄	1	1	0	6.03	[120]
2	25	NaClO ₄	1	1	0	6.2	[119]
3	25	NaClO ₄	1	1	0	6.39	

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3	25	NaClO ₄	1	1	0	6	
5	25	NaClO ₄	1	1	0	6.5	
7	25	NaClO ₄	1	1	0	6.55	[121]
9	25	NaClO ₄	1	1	0	7.34	
1	25	KNO ₃	1	1	0	5.66	[87]
0.1	25	KCl	1	1	0	6.7	[126]
0	25	NaCl	1	1	0	6	[116]
0.3	25	NaCl	1	1	0	5.94	
1	25	NaCl	1	1	0	5.92	
2	25	NaCl	1	1	0	5.89	[122]
3	25	NaCl	1	1	0	6.61	
4	25	NaCl	1	1	0	6.7	
5	25	NaCl	1	1	0	5.82	
1	25	NaClO ₄	1	2	0	10.55	[128]
3	25	NaClO ₄	1	2	0	11.52	
3	25	NaClO ₄	1	2	0	11.21	[118]
0	25	NaCl	1	2	0	11.8	
0.1	25	NaClO ₄	1	2	0	11.08	[115]
0.1	20	NaClO ₄	1	2	0	8.69	[92]
0.1	20	NaClO ₄	1	2	0	10.59	[123]
1	20	NaClO ₄	1	2	0	10.64	
1	25	NaClO ₄	1	2	0	10.87	[120]
2	25	NaClO ₄	1	2	0	11.21	[119]
3	25	NaClO ₄	1	2	0	11.52	
3	25	NaClO ₄	1	2	0	11.2	
5	25	NaClO ₄	1	2	0	11.28	
7	25	NaClO ₄	1	2	0	12.94	[121]

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9	25	NaClO ₄	1	2	0	14.08	
0.2	30	NaClO ₄	1	2	0	8.63	[87]
1	25	KNO ₃	1	2	0	9.66	[126]
0.1	25	KCl	1	2	0	11.8	[116]
0	25	NaCl	1	2	0	10.44	
0.3	25	NaCl	1	2	0	10.1	[119]
2	25	NaCl	1	2	0	10.2	[122]
3	25	NaCl	1	2	0	11	
1	25	NaClO ₄	1	3	0	13.02	[128]
3	25	NaClO ₄	1	3	0	13.41	
3	25	NaClO ₄	1	3	0	13.8	[118]
0	25	NaCl	1	3	0	13.96	
0.1	20	NaClO ₄	1	3	0	12	[92]
1	20	NaClO ₄	1	3	0	11	[123]
1	25	NaClO ₄	1	3	0	14	[120]
2	25	NaClO ₄	1	3	0	14.9	[119]
3	25	NaClO ₄	1	3	0	15.2	
1	25	NaClO ₄	1	1	-1	1.39	[128]
3	25	NaClO ₄	1	1	-1	0.81	
1	25	NaClO ₄	2	4	-2	11.05	
3	25	NaClO ₄	2	4	-2	12	
1	25	NaClO ₄	2	2	-4	-8.34	
3	25	NaClO ₄	2	3	0	18.5	[118]
3	25	NaClO ₄	2	5	0	28.5	
1	10	NaClO ₄	1	1	1	4.47	[129]
1	25	NaClO ₄	1	1	1	4.58	
0.996	40	NaClO ₄	1	1	1	4.4.64	

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	0.986	55	NaClO ₄	1	1	1	4.70	
	0.978	70	NaClO ₄	1	1	1	4.81	
oda	0	25	NaCl	1	1	0	6.146	[109]
	0.1	25	NaCl	1	1	0	5.289	
	0.25	25	NaCl	1	1	0	5.025	
	0.5	25	NaCl	1	1	0	4.836	
	0.75	25	NaCl	1	1	0	4.744	
	1	25	NaCl	1	1	0	4.694	
	0	25	NaCl	1	1	-1	0.196	
	0.1	25	NaCl	1	1	-1	-0.46	
	0.25	25	NaCl	1	1	-1	-0.678	
	0.5	25	NaCl	1	1	-1	-0.853	
	0.75	25	NaCl	1	1	-1	-0.956	
	1	25	NaCl	1	1	-1	-1.027	
	0	25	NaCl	1	2	0	8.36	
	0.1	25	NaCl	1	2	0	7.47	
	0.25	25	NaCl	1	2	0	7.15	
	0.5	25	NaCl	1	2	0	6.88	
	0.75	25	NaCl	1	2	0	6.7	
	1	25	NaCl	1	2	0	6.57	
	0	25	NaCl	2	2	-2	3.53	
	0.1	25	NaCl	2	2	-2	2.41	
	0.25	25	NaCl	2	2	-2	2.01	
	0.5	25	NaCl	2	2	-2	1.66	
	0.75	25	NaCl	2	2	-2	1.43	
	1	25	NaCl	2	2	-2	1.26	
	0	25	NaCl	2	2	-1	8.97	

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	0.1	25	NaCl	2	2	-1	7.48	
	0.25	25	NaCl	2	2	-1	7.05	
	0.5	25	NaCl	2	2	-1	6.77	
	0.75	25	NaCl	2	2	-1	6.65	
	1	25	NaCl	2	2	-1	6.61	
	0.1	25	KNO ₃	1	1	0	5.235	
	0.1	25	KNO ₃	1	1	-1	-0.46	
	0.1	25	KNO ₃	1	2	0	7.56	
	0.1	25	KNO ₃	2	2	-2	2.26	
	0.1	25	KNO ₃	2	2	-1	7.45	
	0.1	25	NaClO ₄	1	1	0	5.11	[100]
	0.1	25	KNO ₃	1	1	0	5.77	[104]
	0.1	25	NaClO ₄	1	2	0	7.54	[103]
	0.1	25	KNO ₃	1	2	0	7.84	[104]
	0.1	25	KNO ₃	2	2	-2	4.29	
toda	0	25	NaCl	1	1	0	3.636	[109]
	0.1	25	NaCl	1	1	0	2.787	
	0.25	25	NaCl	1	1	0	2.535	
	0.5	25	NaCl	1	1	0	2.366	
	0.75	25	NaCl	1	1	0	2.294	
	1	25	NaCl	1	1	0	2.264	
	0	25	NaCl	1	1	1	6.65	
	0.1	25	NaCl	1	1	1	5.787	
	0.25	25	NaCl	1	1	1	5.514	
	0.5	25	NaCl	1	1	1	5,31	
	0.75	25	NaCl	1	1	1	5,203	
	1	25	NaCl	1	1	1	5,138	

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	0	25	NaCl	1	1	-1	-1,242	
	0.1	25	NaCl	1	1	-1	-1,884	
	0.25	25	NaCl	1	1	-1	-2.08	
	0.5	25	NaCl	1	1	-1	-2.22	
	0.75	25	NaCl	1	1	-1	-2.286	
	1	25	NaCl	1	1	-1	-2.321	
tca	0	25	NaCl	1	1	0	6.222	[108]
	0.1	25	NaCl	1	1	0	4.984	
	0.25	25	NaCl	1	1	0	4.676	
	0.5	25	NaCl	1	1	0	4.538	
	0.75	25	NaCl	1	1	0	4.547	
	1	25	NaCl	1	1	0	4.617	
	0	25	NaCl	1	1	1	11.251	
	0.1	25	NaCl	1	1	1	9.737	
	0.25	25	NaCl	1	1	1	9.257	
	0.5	25	NaCl	1	1	1	8.895	
	0.75	25	NaCl	1	1	1	8.704	
	1	25	NaCl	1	1	1	8.586	
	0	25	NaCl	1	2	0	7.75	
	0.1	25	NaCl	1	2	0	7.2	
	0.25	25	NaCl	1	2	0	7.14	
	0.5	25	NaCl	1	2	0	7.22	
	0.75	25	NaCl	1	2	0	7.37	
	1	25	NaCl	1	2	0	11.04	
	0	25	NaCl	1	2	1	14,33	
	0.1	25	NaCl	1	2	1	12,67	
	0.25	25	NaCl	1	2	1	12,11	

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	0.5	25	NaCl	1	2	1	11,62	
	0.75	25	NaCl	1	2	1	11,29	
	1	25	NaCl	1	2	1	11.04	
btc	0	25	NaCl	1	1	0	7.94	[107]
	0.1	25	NaCl	1	1	0	6.25	
	0.25	25	NaCl	1	1	0	5.76	
	0.5	25	NaCl	1	1	0	5.44	
	0.75	25	NaCl	1	1	0	5.31	
	1	25	NaCl	1	1	0	5.27	
	0	25	NaCl	1	1	1	13.08	
	0.1	25	NaCl	1	1	1	10.95	
	0.25	25	NaCl	1	1	1	10.32	
	0.5	25	NaCl	1	1	1	9.88	
	0.75	25	NaCl	1	1	1	9.68	
	1	25	NaCl	1	1	1	9.59	
	0	25	NaCl	1	1	2	17.4	
	0.1	25	NaCl	1	1	2	15.03	
	0.25	25	NaCl	1	1	2	14.29	
	0.5	25	NaCl	1	1	2	13.75	
	0.75	25	NaCl	1	1	2	13.47	
	1	25	NaCl	1	1	2	13.3	
	0	25	NaCl	1	1	-1	2.11	
	0.1	25	NaCl	1	1	-1	1.01	
	0.25	25	NaCl	1	1	-1	0.63	
	0.5	25	NaCl	1	1	-1	0.32	
	0.75	25	NaCl	1	1	-1	0.13	
	1	25	NaCl	1	1	-1	-0.02	

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mellitate	0	25	NaCl	1	1	0	10.155	[110]
	0.1	25	NaCl	1	1	0	7.764	
	0.25	25	NaCl	1	1	0	7.167	
	0.5	25	NaCl	1	1	0	6.785	
	0.75	25	NaCl	1	1	0	6.588	
	1	25	NaCl	1	1	0	6.449	
	0	25	NaCl	1	1	1	16.084	
	0.1	25	NaCl	1	1	1	12.784	
	0.25	25	NaCl	1	1	1	11.851	
	0.5	25	NaCl	1	1	1	10.165	
	0.75	25	NaCl	1	1	1	10.768	
	1	25	NaCl	1	1	1	10.473	
	0	25	NaCl	1	1	2	20.749	
	0.1	25	NaCl	1	1	2	16.714	
	0.25	25	NaCl	1	1	2	15.432	
	0.5	25	NaCl	1	1	2	14.336	
	0.75	25	NaCl	1	1	2	13.585	
	1	25	NaCl	1	1	2	12.96	
	0	25	NaCl	1	1	3	24.038	
	0.1	25	NaCl	1	1	3	19.638	
	0.25	25	NaCl	1	1	3	18.265	
	0.5	25	NaCl	1	1	3	17.042	
	0.75	25	NaCl	1	1	3	16.137	
	1	25	NaCl	1	1	3	15.329	
	0	25	NaCl	2	1	0	17.936	
	0.1	25	NaCl	2	1	0	13.808	
	0.25	25	NaCl	2	1	0	12.612	

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	0.5	25	NaCl	2	1	0	11.667	
	0.75	25	NaCl	2	1	0	11.05	
	1	25	NaCl	2	1	0	10.543	
	0	25	NaCl	1	1	-1	2.327	
	0.1	25	NaCl	1	1	-1	0.938	
	0.25	25	NaCl	1	1	-1	0.6	
	0.5	25	NaCl	1	1	-1	0.396	
	0.75	25	NaCl	1	1	-1	0.303	
	1	25	NaCl	1	1	-1	0.245	
	0	25	NaCl	1	1	-2	-6.804	
	0.1	25	NaCl	1	1	-2	-6.916	
	0.25	25	NaCl	1	1	-2	-6.862	
	0.5	25	NaCl	1	1	-2	-6.768	
	0.75	25	NaCl	1	1	-2	-6.698	
	1	25	NaCl	1	1	-2	-6.647	
citrate	0	25	NaCl	1	1	0	9.02	[160]
	0.1	25	NaCl	1	1	0	7.704	
	0.25	25	NaCl	1	1	0	7.262	
	0.5	25	NaCl	1	1	0	6.901	
	0.75	25	NaCl	1	1	0	6.686	
	1	25	NaCl	1	1	0	6.533	
	0	25	NaCl	2	2	0	21.82	
	0.1	25	NaCl	2	2	0	19.414	
	0.25	25	NaCl	2	2	0	18.615	
	0.5	25	NaCl	2	2	0	17.97	
	0.75	25	NaCl	2	2	0	17.594	
	1	25	NaCl	2	2	0	17.333	

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0	25	NaCl	2	2	-2	9.112
0.1	25	NaCl	2	2	-2	8.233
0.25	25	NaCl	2	2	-2	7.936
0.5	25	NaCl	2	2	-2	7.691
0.75	25	NaCl	2	2	-2	7.544
1	25	NaCl	2	2	-2	7.438
0	25	NaCl	2	2	-1	15.779
0.1	25	NaCl	2	2	-1	14.023
0.25	25	NaCl	2	2	-1	13.433
0.5	25	NaCl	2	2	-1	12.95
0.75	25	NaCl	2	2	-1	12.662
1	25	NaCl	2	2	-1	14,458
0	25	NaCl	2	1	-2	5,462
0.1	25	NaCl	2	1	-2	3.907
0.25	25	NaCl	2	1	-2	3.363
0.5	25	NaCl	2	1	-2	2.893
0.75	25	NaCl	2	1	-2	2.594
1	25	NaCl	2	1	-2	2.368
0	25	NaCl	2	1	-1	9.713
0.1	25	NaCl	2	1	-1	7.948
0.25	25	NaCl	2	1	-1	7.344
0.5	25	NaCl	2	1	-1	6.838
0.75	25	NaCl	2	1	-1	6.527
1	25	NaCl	2	1	-1	6.299
0	25	NaCl	3	2	-5	-1.98
0.1	25	NaCl	3	2	-5	-1.993
0.25	25	NaCl	3	2	-5	-2.013

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0.5	25	NaCl	3	2	-5	-2.046	
0.75	25	NaCl	3	2	-5	-2.079	
1	25	NaCl	3	2	-5	-2.112	
0.1	25	KNO ₃	1	1	0	7.84	
0.1	25	KNO ₃	2	2	0	19.26	
0.1	25	KNO ₃	2	2	-2	8.87	
0.1	25	KNO ₃	2	2	-1	14.05	
0.1	25	KNO ₃	2	1	-2	3.62	
0.1	25	KNO ₃	2	1	-1	7.88	
0.1	25	KNO ₃	3	2	-5	-0.92	
0.15	25	NaCl	1	1	0	8.5	[168]
0.1	25	KNO ₃	1	1	0	7.4	[157]
1	25	KNO ₃	1	1	0	6.87	
1	25	KNO ₃	1	1	0	5.78	[168]
0.1	25	NaCl	1	1	0	7.22	[147]
1	25	NaCl	1	1	0	6.2	[146]
1	25	NaCl	1	1	0	7.17	
0.3	25	NaCl	1	1	0	7.3	[145]
1	25	NaCl	1	1	0	7.08	
2	25	NaCl	1	1	0	7.22	
3	25	NaCl	1	1	0	7.1	
4	25	NaCl	1	1	0	7.02	
5	25	NaCl	1	1	0	7.03	
0.1	21	NaClO ₄	1	1	0	6.69	[141]
0.136	25	KNO ₃	2	2	0	19.26	[133]
0.1	25	KNO ₃	2	2	0	18.87	[157]
1	25	KNO ₃	2	2	0	17.7	

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	0.15	25	NaCl	2	2	0	18.9	[168]
	1	25	KNO ₃	2	2	0	17.57	
	1	25	NaCl	2	2	0	17	[146]
formate	1	20	NaClO ₄	1	1	0	1.89	[92]
	1	20	NaClO ₄	1	1	0	1.83	[105]
	1	20	NaClO ₄	1	2	0	3.13	
	0.1	25	NaClO ₄	1	1	0	3.54	[113]
	1	20	NaClO ₄	1	3	0	3.52	
lactate	1	20	NaClO ₄	1	1	0	2.43	[92]
	1	20	NaClO ₄	1	2	0	4.49	
	1	20	NaClO ₄	1	3	0	6.36	
	0.3	25	NaCl	1	1	0	2.6	[82]
	1	25	NaCl	1	1	0	2.36	
	2	25	NaCl	1	1	0	2.45	
	3	25	NaCl	1	1	0	2.73	
	4	25	NaCl	1	1	0	2.5	
	5	25	NaCl	1	1	0	2.64	
maleate	1	25	KNO ₃	1	1	0	4.46	[87]
propionate	1	20	NaClO ₄	1	1	0	2.53	[87]
	1	20	NaClO ₄	1	2	0	4.68	
	1	20	NaClO ₄	1	3	0	10.22	
	0.1	25	NaClO ₄	1	1	0	4.71	[113]
phthalate	1	25	KNO ₃	1	1	0	4.38	[87]
butyrate	1	20	NaClO ₄	1	1	0	2.58	[105]
	1	20	NaClO ₄	1	2	0	4.71	
	1	20	NaClO ₄	1	3	0	6.91	
isobutyrate	1	20	NaClO ₄	1	1	0	2.48	[105]

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1	20	NaClO ₄	1	2	0	4.87
1	20	NaClO ₄	1	3	0	7.20

^{a)} oda = diglycolic acid, toda = diethylenetrioxodiacetic acid, tca = 1,2,3-propanetricarboxylates, btc = 1,2,3,4-butanetetracarboxylate, mellitate = 1,2,3,4,5,6-benzenehexacarboxylate

Table 2S Literature values of uranyl-amino acid stability constant complexes

Aminoacid	<i>I</i> /mol L ⁻¹	<i>t</i> /°C	medium	log β_{111}	log β_{122}	log β_{110}	log β_{120}	Ref.
glycine	0.1	22	NaClO ₄	10.84	21.19			[188]
	0.5	22	NaClO ₄	10.79(4)	20.93(1)			
	0.1–1	25	NaClO ₄	7.89–7.52	9.62-9.35			[184]
	0.1-1	25	NaCl	7.81–7.19	9.77-9.57			
	0.1	30	KCl			7.53	14.68	[179, 221]
	1	25	NaClO ₄			9.43	17.55	[193, 194]
	0.5	26	NaClO ₄	1.34 ^{a)}	2.72 ^{b)}			[180, 221]
	0.45	25	NaCl	1.43 ^{a)}				[93]
	?	?	?			8.62		[181, 221]
	0.1	30	NaClO ₄		2.14 ^{b)}			[204, 221]
	1	25	NaClO ₄	1.16 ^{a)}	2.20 ^{b)}			[102]
	0.1	30	KNO ₃	2.08 ^{a)}				[215]
	α -alanine	0.1	25	KNO ₃			7.33	14.97
0.2		25	KNO ₃			7.79	15.18	[213]
0.5		26	NaClO ₄	2.04 ^{a)}	2.08 ^{b)}			[180, 222] ^{c)}
0.1		30	NaClO ₄		2.15 ^{b)}			[204, 222]
0.1		30	KNO ₃	2.05 ^{a)}				[215]

	0.1	30	NaClO ₄	2.03 ^{a)}			[203, 222]
	0.1	25	NaClO ₄			8.55	[205, 222]
	?	?	?			9.00	[181, 222]
	0.5	25		7.0			[211]
α-aminobutyrate	0.1	30	NaClO ₄		2.12 ^{b)}		[204]
	0.1	30	NaClO ₄	1.99 ^{a)}			[203]
α-aminoisobutyrate	0.1	30	NaClO ₄	1.85 ^{a)}			[203]
	0.1	25	NaClO ₄			7.72	[205]
	1	22	NaClO ₄	1.30-1.36 ^{a)}	1.83-2.07 ^{b)}		[155]
L-leucine	0.1	35	KNO ₃	2.03-2.05 ^{a)}			[174]
	0.1	25	KNO ₃			7.13	[199, 216, 222]
	?	?	?			8.60	[181, 222]
L-isoleucine	0.1	25	KNO ₃			7.02	[199, 216]
	0.1	25	KNO ₃	1.87-2.04 ^{a)}			[215]
2-aminohexanoate	0.1	20-40	NaClO ₄			7.81-7.61	[207, 222]
valine	0.1	25	KNO ₃			7.10	[199, 216, 222]
	0.1	30	KNO ₃	1.98-2.04 ^{a)}			[215]
	0.1	30	NaClO ₄	2.01 ^{a)}			[203, 219, 222]
	0.1	31	NaClO ₄			7.97	[205, 219, 222]

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	?	?	?			8.60		[181, 222]
	0.1	35	NaClO ₄			8.02	14.53	[222, 227]
DL-β-phenyl alanine	0.1	35	KNO ₃	1.74-1.76 ^{a)}				[174]
	0.1	25	KNO ₃			6.77	13.91	[199]
	0.1	30	NaClO ₄	1.84 ^{a)}				[203]
	0.1	31	NaClO ₄			7.98		[205]
β-alanine	1	25	NaClO ₄	1.93 ^{a)}	3.44 ^{b)}			[178, 222] ^{d)}
	0.1	30	KCl			7.78	15.31	[179, 222]
	0.1	30	NaClO ₄		3.49 ^{b)}			[204, 219, 222]
	0.2	25	KNO ₃			7.70	14.79	[213]
	0.1	30	NaClO ₄	2.44 ^{a)}				[203, 222]
	?	?	?			9.92		[181, 222]
	0.1	30	NaClO ₄			9.20		[201, 222]
	0.5	25				7.93–7.86		[211, 222]
β-aminoisobutyrate	0.1	30	NaClO ₄	2.39 ^{a)}				[203]
γ-aminobutyrate	1	25	NaClO ₄	2.25 ^{a)}	4.02 ^{b)}			[178] ^{e)}
	0.1	30	NaClO ₄		4.44 ^{b)}			[204, 219]
	0.1	30	NaClO ₄	2.43 ^{a)}	4.58 ^{b)}			[203, 219]
aspartate	1	25	NaClO ₄	2.41 ^{a)}	4.14 ^{b)}			[176]
	0.1	30	NaClO ₄			8.71		[212, 219]

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	0.5	25	?			8.62-8.40		[211]
	0.1	30-50	NaClO ₄			8.34-10.4	8.8 ^{e)}	[225]
	0.2	25	KNO ₃	2.61 ^{a)}				[80, 219]
	0.1	30	KCl			8.00		[179]
	0.1-1.0	25	NaCl	12.64-12.30		7.59-7.30		[186] ^{d)}
	→ 0	25		13.42		8.37		
	1	25	NaClO ₄	13.22	24.97			[193]
	0.1	25	KNO ₃			6.89		[217]
glutamate	0.1	30	NaClO ₄			8.43		[212, 219]
	0.1	25	KNO ₃			8.23	14.87	[187, 219]
	0.2	25	KNO ₃	2.66 ^{a)}				[80, 219]
	0.1-1.0	25	NaCl	12.75-12.66		7.75-7.63		[186] ^{g)}
	→ 0	25		13.60		8.53		
	1	25	NaClO ₄	13.41	25.05			[193]
L-threonine	0.1	35	KNO ₃	1.96-2.01 ^{a)}				[174]
	0.1	25	KNO ₃			6.65	12.08	[199, 220]
	0.1	30	NaClO ₄			7.30	14.20	[201, 220]
	0.05-0.25	25	KCl			6.35-6.22	12.50-12.26	[208, 220]

	0.05-0.25	45	KCl			6.12–5.95	12.04–11.65	
	0.5	25				6.00–5.95		[211, 220]
L-asparagine	0.1	35	KNO ₃	1.83-1.78 ^{a)}				[174]
	1	25	NaClO ₄			8.84	15.61	[193]
	0.1	25	KNO ₃			8.12		[217]
	0.1	31	NaClO ₄			7.23		[205, 219, 220]
	?	?	?			6.88		[181, 220]
	0.1	25	NaClO ₄			6.95-6.79	6.16-6.00 ^{h)}	[228]
histidine	0.15-0.25	25				7.71		[195, 219]
	0.5	26	NaClO ₄	1.45 ^{a)}				[180]
	0.1	35				8.70	14.05	[247]
serine	0.1	30	KNO ₃	1.89-1.83 ^{a)}				[215]
	0.1-1	25	NaClO ₄	1.22–0.34 ^{a)}	2.36–2.25 ^{b)}			[182]
	→ 0			1.32 ^{a)}	2.74 ^{b)}			
	0.1	25	KNO ₃			8.66	14.66	[216, 220]
	1	25	NaClO ₄			9.01	17.09	[193]
	0.1	25	KNO ₃			8.41		[217]
	~0.02	25	?			6.86		[181, 220]
	1	30	NaClO ₄			7.60	14.75	[201, 220]
lysine	1	25	NaClO ₄	18.85				[193]
	0.1	20-40	NaClO ₄			7.90-7.81	14.90-13.71	[223, 320]
DL-Tryptophan	0.1	30	NaClO ₄	1.83 ^{a)}				[203]
cysteine	0.1	22	NaClO ₄				20.05 ⁱ⁾	[188]

	0.5	22	NaClO ₄	15.28	19.28 ⁱ⁾			
	0.1	25	KNO ₃			5.84	11.85	[199, 216, 220]
	0.1	30	NaClO ₄			9.04		[200, 201, 220]
D-methionine	0.1	15-30	KNO ₃	13.80–13.65	22.50–22.20			[189, 220]
	0.1	25	KNO ₃			6.41	13.38	[199, 216, 220]
	0.1	30	NaClO ₄			7.65	13.95	[200, 201, 220]
L-Glutamine	0.1	25-45	KCl			6.52–6.14	11.88–11.24	[210, 220]
	0.1	35	KNO ₃			7.05–7.00	13.90–13.73	[209]
	0.1–0.3	35	KNO ₃			7.05–6.95	13.90–13.70	
glycylglycine	0.1	25	NaClO ₄			6.63-6.85	6.00-6.22 ^{h)}	[228]
	1	25	NaClO ₄	1.61 ^{a)}	2.99 ^{b)}			[177]
	0.1	31	NaClO ₄			6.72		[205, 219]
glutathione	1	25	NaClO ₄			2.24		[177]
dipicolinate	0.1	25	KNO ₃			5.70		[217]
N-acetyl glycine	0.1	30	NaClO ₄			3.30		[200, 201]
L-Proline	?	?	?			10.45		[181]

^{a)} refers to the equilibrium: $\text{UO}_2^{2+} + \text{HL} = (\text{UO}_2)(\text{HL})^{2+}$; ^{b)} refers to the equilibrium: $\text{UO}_2^{2+} + 2\text{HL} = (\text{UO}_2)(\text{HL})_2^{2+}$; ^{c)} the authors report also the $\log\beta_{\text{ML}_4} = 3.85$ probably referred to the reaction: $\text{UO}_2^{2+} + 4\text{L} = (\text{UO}_2)\text{L}_4^{2-}$; ^{d)} the authors report also the $\log\beta_{\text{M}(\text{HL})_3} = 4.82$ referred to the reaction: $\text{UO}_2^{2+} + 3\text{HL} = (\text{UO}_2)(\text{HL})_3^{2+}$; ^{e)} the authors report also the $\log\beta_{(\text{UO}_2)(\text{HL})_3} = 6.08$ referred to the reaction: $\text{UO}_2^{2+} + 3\text{HL} = (\text{UO}_2)(\text{HL})_3^{2+}$; ^{e)} $\log K_{\text{ML}_2}$ calculated at $t = 50^\circ\text{C}$; ^{f)} the authors also report a $1.73 \leq \log\beta_{(\text{UO}_2)_2\text{L}(\text{OH})_2} \leq 1.99$ in the ionic strength reported in Table and $\log\beta_{(\text{UO}_2)_2\text{L}(\text{OH})_2} = 2.98$ at I

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= 0 mol L⁻¹; ^{g)} the authors also report a $1.95 \leq \log\beta_{(\text{UO}_2)_2\text{L}(\text{OH})_2} \leq 2.24$ in the ionic strength reported in the Table and $\log\beta_{(\text{UO}_2)_2\text{L}(\text{OH})_2} = 3.31$ at $I = 0$ mol L⁻¹; ^{h)} $\log K_{(\text{UO}_2)\text{L}_2}$ refers to the equilibrium: $(\text{UO}_2)\text{L} + \text{L} = (\text{UO}_2)\text{L}_2^0$; ⁱ⁾ $\log\beta_{(\text{UO}_2)\text{LH}_2}$; the authors report also the $\log\beta_{(\text{UO}_2)\text{L}_3} = 3.90$

Table 3S. Literature values of thermodynamic parameters of uranyl-amino acid complexes

Amino acid	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	medium	species	$\Delta G^{\text{a)}}$	$\Delta H^{\text{a)}}$	$\Delta S^{\text{b)}}$	Ref.
glycine	1	25	NaClO ₄	111		3.9	35	[102]
	1	25	NaClO ₄	122		4.8	58	
L-leucine	0.1	25-45	KCl	110		-59.8		[210, 222]
	0.1	25-45	KCl	120		-114.2		
β -alanine	1	25	NaClO ₄	111		6.5	59	[178, 222] ^{d)}
	1	25	NaClO ₄	122		12.0	106	
	1	25	NaClO ₄	133		11.3	130	
γ -aminobutyrate	1	25	NaClO ₄	111		10.06	79	[178] ^{e)}
	1	25	NaClO ₄	122		15.5	129	
	1	25	NaClO ₄	133		13.0	160	
aspartate	1	25	NaClO ₄	111		8.9	76	[176]
	1	25	NaClO ₄	122		10.5	114	
	0.1	30	NaClO ₄	110	-11.53	-25.996	-47.67	[225]
L-threonine	0.05	25	KCl	110		-20.88	51.5	[208, 220]
	0.05	25	KCl	120		-41.76	99.2	
D-methionine	0.1	25	KCl	110		-35	9.2	[210, 220]
	0.1	25	KCl	120		-58	32.9	
glycylglycine	1	25	NaClO ₄	111		7.08	54	[177]
	1	25	NaClO ₄	122		11.5	96	
	1	25	NaClO ₄	133		14.7	124	
glutathione	1	25	NaClO ₄	111		12.6	85	[177]

^{a)} In kJ mol⁻¹; ^{b)} in J mol⁻¹K⁻¹

Table 4S. Literature values of the uranyl-poly(amino carboxylate) stability constant complexes

Complexones	<i>I</i> /mol L ⁻¹	<i>t</i> /°C	medium	logβ ₁₁₃	logβ ₁₁₂	logβ ₁₁₁	logβ ₁₁₀	logβ ₂₁₀	Ref.
TTHA	0.7	25	NaCl	28.405	24.728	19.138	12.121		[238]
	0.1	25	KNO ₃	31.57	27.57	22.4			[243, 253] ^{a)}
	0.5	25	NaClO ₄		24.64		12.55		[242]
DTPA	0.7	25	NaCl		22.144	17.861	11.789	3.090 ^{b)}	[238]
	0.1	25	KNO ₃		23.71	19.2		19.0	[243, 253] ^{e)}
	0.1	30	NaClO ₄	26.9		18.8			[241] ^{d)}
	0.1	25	NaClO ₄	26.1	23.65	19.5	14.0	19.5	[235]
EDTA	0.7	25	NaCl			15.19	9.810	3.58 ^{b)}	[238]
	0.1-1	25	KNO ₃			7.40-7.35 ^{e)}		17.87-17.77	[236, 237]
	3	25	NaClO ₄			18.59	15.65	20.24	[234]
	0.15	25	NaClO ₄			7.90-7.79 ^{e)}		17.85-17.69	[231]
	0.3-5 ^{d)}	25	NaCl			15.81-15.10	10.72-9.82		[245]
	0	25	-			18.14	12.98		
	0.1	25	KNO ₃			17.16	11.4	17.8	[243] ^{g)}
	0.1	24	R ₄ NX				10.4	15.2	[255]
EGTA	0.1	35	NaClO ₄			7.32 ^{e)}			[248]
	0.7	25	NaCl			17.346	11.597	2.770 ^{b)}	[238]
	0.1	25	KNO ₃			9.41 ^{e)}		17.66	[237]
	0.1	25	KNO ₃				11.23		[226] ^{h)}
	0.2	25	NaClO ₄			9.84 ^{e)}		19.03	[232]
DCTA	0.1	20	NaClO ₄			5.27 ^{e)}			[248]
EDDA	3	25	NaClO ₄				16.02		[234]
	0.1	25	KNO ₃				11.41		[237]
	1	25	NaClO ₄				11.5		[233]
	1	25	NaClO ₄	20.80			11.63		[244]
IDA	3	25	NaClO ₄				9.63		[234]
	0.1	25	KNO ₃				8.73		[226, 253] ⁱ⁾

	0.1-1	25	KNO ₃				8.93-8.73		[246, 253]
	1	20	NaClO ₄				8.66		[100, 253]
	1	25	NaClO ₄			11.19	8.78		[103] ^{b)}
MIMDA	0.1	25	KNO ₃				9.70		[237]
HIMDA	0.1	25	KNO ₃				8.34		[237]
	0.1-1	25	KNO ₃				8.32 – 7.99		[246]
HEDTA ^{m)}	0.2	25	NaClO ₄			6.33 ^{e)}		16.70	[232]
HADA	0.1	25	KNO ₃				6.89		[217]
S,S-EDDS	-	25	-			15.6	10.7		[240] ⁿ⁾
	0.1	30	KNO ₃				10.6		[249]
NTA	0.7	25	NaCl			12.27	8.21	2.39 ^{b)}	[238]
	3	25	NaClO ₄			12.19			[234] ^{o)}
	0.1	20	NaClO ₄				9.56		[248, 252]
	0.1	20	?				7.88		[252]
	0.1	35	?				9.85		[247]
CEDTA	0.1	25	KNO ₃	23.04	20.11	17.06		16.53	[250] ^{p)}
DBT	0.1	25	KNO ₃	25.00	22.25	19.39	13.64	18.61	[250] ^{q)}
OTC	0.1	25	KNO ₃	25.17	22.96	19.91	14.14	19.22	[250] ^{r)}
LTC	0.1	25	KNO ₃	25.32	23.17	20.05	14.27	19.42	[250] ^{s)}

^{a)} other species $\log\beta_{212} = 31.77$, $\log\beta_{211} = 27.95$, $\log\beta_{21-1} = 16.62$; ^{b)} $\log\beta_{11-1}$; ^{c)} other species $\log\beta_{211} = 23.8$, $\log\beta_{21-1} = 13.52$, $\log\beta_{21-2} = 7.54$; ^{d)} other species $\log\beta_{213} = 31.2$, $\log\beta_{211} = 22.9$; ^{e)} $\log K_{111}$; ^{f)} mol kg⁻¹ (H₂O); ^{g)} other species $\log\beta_{21-1} = 12.42$, $\log\beta_{21-2} = 6.84$; ^{h)} other species $\log\beta_{120} = 19.03$; ⁱ⁾ other species $\log\beta_{120} = 17.28$; ^{j)} other species: $\log\beta_{121} = 19.81$, $\log\beta_{122} = 22.50$; ^{m)} Lai *et al.* [251] also reported the follow stability constants: $\log K_{124} = 5.57$, $\log K_{122} = 5.73 - 7.13$ and $\log K_{120} = 8.61-9.81$; ⁿ⁾ extrapolated values; ^{o)} other species $\log\beta_{122} = 23.8$; ^{p)} other species: $\log\beta_{220} = 26.27$, $\log\beta_{211} = 19.99$, $\log\beta_{21-1} = 10.63$, $\log\beta_{42-2} = 26.32$, $\log\beta_{42-4} = 15.31$; ^{q)} other species: $\log\beta_{11-1} = 7.33$, $\log\beta_{220} = 29.62$, $\log\beta_{211} = 22.16$, $\log\beta_{21-1} = 13.15$, $\log\beta_{21-2} = 7.62$, $\log\beta_{42-2} = 30.12$, $\log\beta_{42-4} = 19.21$ ^{r)} other species: $\log\beta_{11-1} = 7.73$, $\log\beta_{220} = 31.34$, $\log\beta_{211} = 22.99$, $\log\beta_{42-2} = 31.86$, $\log\beta_{42-4} = 20.86$; ^{s)} other species: $\log\beta_{11-1} = 7.73$, $\log\beta_{220} = 31.03$, $\log\beta_{211} = 23.08$, $\log\beta_{210} = 19.42$, $\log\beta_{42-2} = 32.30$, $\log\beta_{42-4} = 21.15$.

Table 5S. Literature values of thermodynamic parameters of the uranyl-poly(amino carboxylate) complexes

Complexones	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	medium	species	$-\Delta G/\text{kJ mol}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1}\text{ mol}^{-1}$	ref.
EDTA	0.1	10-40	?	$(\text{UO}_2)(\text{HL})$		12	188	[40]
EGTA	0.1	20-40	?	$(\text{UO}_2)(\text{HL})$		8	209	[40]
EDDA	0.1	20-40	?	$(\text{UO}_2)\text{L}$		8	238	[40]
IDA	1	25	NaClO_4	$(\text{UO}_2)\text{L}$	50.12	-2.2	161	[103]
	1	25	NaClO_4	$(\text{UO}_2)\text{LH}$	63.9	-30.8	111	
	1	25	NaClO_4	$(\text{UO}_2)\text{L}_2\text{H}$	113.1	-50	211	
	1	25	NaClO_4	$(\text{UO}_2)\text{L}_2\text{H}_2$	128.4	-52	255	

Table 6S Literature values of uranyl-humate and -fulvate complexes

ligand	model	medium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	pH	$\log\beta_{110}$	$\log\beta_{120}$	Ref.
HA (natural and synthetic)	MICNM ^{a)}	NaClO ₄	0.1	20	4	6.10 - 6.61		[296]
HA	MICNM	NaCO ₄	0.1 - 4 · 10 ⁻³	25	4-5	6.08		[290]
HA	MICNM	NaClO ₄	0.1		7	6.33		[298]
HA	MICNM	NaClO ₄	0.1	22	4	6.16		[281]
HA	PM ^{b)}	?	?	?	4	5.11		[304]
HA	MICNM	?	?	?	4	6.2		
HA (synthetic)	MICNM	NaClO ₄	0.1	?	3.9	5.85 - 6.16		[295]
HA	MSRW ^{c)}	NaClO ₄	0.1	25	4	4.58 - 4.70 ^{d)}	5.05 - 5.07 ^{d)}	[302, 303]
HA	MS ^{e)}	NaCl	0.01	?	2-9	4.72 ^{d)}	6.73 ^{d)}	[288]
FA	MS	NaCl	0.01	?	2-9	5.56 ^{d)}	7.43 ^{d)}	
HA	DMM and CMM ^{f)}	?	0.01	?	4.5	6.5		[284]
HA	-	NaClO ₄	0.1	room t	7.5 – 7.9	6.2		[294] ^{g)}
FA	1:n (Shubert)	NaClO ₄	0.1	21	4-5	5.37-5.15	(n = 1.28-1.14)	[141]
HA	1:n (Shubert)	NaClO ₄	0.1	21	4-5	6.75-7.57	(n = 1.46-1.44)	
FA	1:1	NaClO ₄	0.1	21	4-5	7.35-7.08		
HA	1:1	NaClO ₄	0.1	21	4-5	7.59-7.64		
HA	1:1	?	low	20	~ 7	5.07 – 6.30 ^{h)}		[297]
FA	1:1	?	low	20	~ 7	5.22 – 5.59		
FA	1:1	KNO ₃	0.1	25	?	3.6 - 5.2		[283]
FA	1:1	?	?	25	3.5	3.93 – 4.4 ⁱ⁾		[282]
FA	1:1	?	?	25	7	4.06 – 4.12 ⁱ⁾		
HA	1:1	NaClO ₄	0.1 – 0.5	25	3.5-7	7.7		[286]
FA	1:1	NaClO ₄	0.02	20	5-10	7.70 - 14.40		[309]
HA	1:1	NaClO ₄	0.02	20	5-10	7.72 - 13.96		
FA	1:1		0.01		5	6.41		[285]
HA	1:1	?	0.02-0.2		5-10	6-12		[306]

HA	1:1	-	→ 0	25	3.5	4.33 - 5.29		[289]
HA	1:1 1:2	-	→ 0	25	3.5	2.63 - 3.87	5.8 - 7.8	
FA	1:1 1:2	NaClO ₄	0.1	25	3.5 4.5	4.7-5.1	8.8-9.6	[291]
HA	1:1 1:2	NaClO ₄	0.1	25	3.5-4.5	4.9-5.2	8.7-9.3	
HA	1:1 1:2	NaClO ₄	0.1	25	4.04	5.11	8.94	[299]
HA	1:1 1:2	NaClO ₄	0.1	2-34	4.04	5.13-5.08	8.85-9.11	
HA	1:1 1:2		0.1		6.5-7.3	4.6-6.5	8.9	[300]
FA	1:1 1:2		0.1		6	4.3-4.8	7.3-8.3	[301]
HA	1:1 1:2	?	?	?	3.3	4.18	7.28	[293]
FA	1:1 1:2	NaClO ₄	0.1	21	4-5	4.23-4.54	7.31-7.45	[141]
HA	1:1 1:2	NaClO ₄	0.1	21	4-5	4.75-5.38	8.39-9.59	[141]
FA	FA ₁ and FA ₂	NaCl	0.1-0.75	25	3 -7	4.85 - 4.05	14.98 - 13.09	[307] ^{b)}
PAA	1:1	NaCl	0.1-0.75	25	3 -7	7.817		[307] ^{b)}
PAA 2 kDa	1:1	NaNO ₃	0.1	25		9.3	n = 2	[287]
PAA 270 KDa		NaNO ₃	0.5			9.5	n=2	[292]
PMA 300 KDa		NaNO ₃	0.5			15.3	n=3	

^{a)} Metal ion charge neutralization model; ^{b)} polyelectrolyte model; ^{c)} multi-site Ryan-Weber model; ^{d)} the two $\log\beta$ regard two different 1:1 complexes of different strength; ^{e)} Multi Site model; ^{f)} CMM and DMM stand for Continuous Multi-ligand and for Discrete Multi-ligand Model, respectively; ^{g)} other species: $\log\beta_{(UO_2)(HA)(OH)} = 1.52$; ^{h)} several HA were studied; ⁱ⁾ mean values obtained at different carbonate concentrations; ^{l)} fulvic acid was considered as constituted by two monomer units: one di-carboxylic unit and one phenolic unit; other species $\log\beta_{UO_2(F A_1)(F A_2)H} = 19.48 - 17.75$; other species $\log\beta_{UO_2(PAA)(OH)} = 1.05$, $\log\beta_{(UO_2)_2(PAA)(OH)_2} = 1.76$.