

Potentiometric and spectrophotometric characterization of the UO_2^{2+} -citrate complexes in aqueous solution, at different concentrations, ionic strengths and supporting electrolytes

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Summary. In this paper we report an investigation on the interactions between dioxouranium(VI) and citrate using potentiometry (H^+ -glass electrode) and UV-spectrophotometry. Potentiometric measurements were carried out in NaCl and KNO_3 aqueous solutions at $t = 25^\circ\text{C}$ in a wide range of experimental conditions (concentrations, ligand/metal molar ratio, pH, titrants). Measurements in NaCl were carried out at different ionic strength values ($0.1 \leq I/\text{mol L}^{-1} \leq 1.0$); different procedures were employed for the acquisition of experimental data and careful analysis of these data performed. In all cases the speciation model that best fits experimental data takes into account the formation of the following species: $\text{UO}_2(\text{Cit})^-$, $(\text{UO}_2)_2(\text{Cit})_2^{2-}$, $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$, $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_3^{3-}$, $(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$, $(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$, $(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$.

The dependence on ionic strength of formation constants was taken into account by using both a simple Debye–Hückel type equation and the SIT (specific ion interaction theory) approach.

Moreover, a visible absorption spectrum for each complex reaching a significant percentage of formation in solution (KNO_3 medium) has been calculated to characterise the compounds found by pH-metric refinement.

Recommended values for the uranyl-citrate species were proposed for each ionic strength value in NaCl aqueous solution. Comparison with literature stability constants is reported too.

1. Introduction

Studies of the coordination chemistry in aqueous solutions of actinides and in particular of uranium are increasingly important for understanding the environment [1–7]. Information about the speciation of actinide in aqueous solution containing different supporting electrolytes are essential for assessing and developing long-term strategies, addressing problems such as migration in nuclear waste repositories,

improvements in the processing of nuclear waste and materials or removing of these metal ions from sediments.

In fact, a method for removing uranium contamination from soils involves extraction using O-donor ligands as chelating agents. These types of extractants are quite efficient in binding the uranyl ion and thus are suitable for removing uranium contamination when it is in the hexavalent uranyl ion form. For example, the uranyl-complexing properties of citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) have been extensively studied [8–36]. Citric acid dramatically increases uranium accumulation in plants and may thus be an important agent in remediation strategies for contaminated soils [37–41].

The presence of citric acid can influence both uranium speciation and the extent of partitioning to mineral surfaces, affecting uranium mobility in the environment [37, 39–41]. One advantage of using citrate rather than other organic ligands is that these complexes are reported to readily biodegrade under alkaline conditions or to photodegrade, and hence subsequent uranium mobility can be controlled [42–46]. Other investigations have however shown that the uranyl-citrate complexes can be resistant to biodegradation at neutral-acidic conditions [46], with the structure of the complex being the dominant factor. When the hydroxyl groups of the citrate are all involved in bonding to U, biodegradation does not occur. Speciation and structural information on the UO_2^{2+} -citrate complexes is important to the development of mechanistic models describing adsorption phenomena affecting transport of uranium in soils and degradation pathways of these complexes.

Several investigations dealing with uranyl(VI)-citrate complex formation, have been produced, by means of different experimental techniques, such as potentiometry, visible and infrared spectroscopy, ionic exchange, ^1H and ^{13}C NMR, electrospray ionization mass spectrometry, EXAFS [8–36]. These papers reported the formation of very stable both mono- and polynuclear species. As regards the type of the species in solution, there is a general agreement on the formation of monomeric $\text{UO}_2(\text{Cit})\text{H}_n^{n-1}$ (with $n = 0, 1, 2, 3$) and dimeric $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_n^{-(n+2)}$ (with $n = 0, 1, 2$) species up to pH 5, while some authors [20, 23, 26] suggested that the buffer region, after pH = 5–6, can be inter-

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preted by assuming the formation of trimeric (or hexameric) species. Nevertheless, in rare cases stability constants for the different protonated species were proposed.

However, despite the investigation of UO_2^{2+} -citrate complexes over a 50-year period, a complete understanding of speciation behavior is lacking, and little structural information is available. The aqueous chemistry of the UO_2^{2+} -citrate system is complex, involving pH-dependent changes in stoichiometry and UO_2^{2+} coordination environment. At low pH (pH = 2–4), the existence of a 2 : 2 dimeric UO_2^{2+} -citrate species is well established, and both the structure and a formation constant have been determined [9, 15, 16].

In order to predict the mobility of uranium in the environment in the presence of chelating agents, it is important to understand the speciation and structure of the complexes formed over a wide range of experimental conditions. Nevertheless till now, a systematic study of the species formed at higher pH values and at different ionic strength values, has not previously been undertaken, and the studies that have been done often produced contradictory conclusions.

The purpose of this study is to characterize the speciation of the UO_2^{2+} -citrate complexes formed in aqueous solutions containing two different supporting electrolytes, namely NaCl and KNO_3 , and to gain an understanding of their behavior at different ionic strengths in a wide range of component concentrations. The difficulties that one can meet in these kind of investigations are related to the fact that citric acid forms different types of complexes with the transition metals and actinides and may involve the formation of bidentate, tridentate, binuclear, or polynuclear complex species.

2. Experimental

2.1 Chemicals

Stock solutions of uranyl nitrate hexahydrate (puriss. > 99.5%), used without further purification, were prepared by dissolving the corresponding Fluka products in ultrapure water and standardized by the gravimetric determination of uranium after oxide U_3O_8 ignition; the concentrations of the stock solutions, prepared daily, varying between 10–50 mmol L^{-1} . Stock solutions of anhydrous citric acids (Fluka puriss. p.a., ACS reagent) were prepared by weighing and then dissolving the solid products in ultrapure water without further purification. The purity was checked by alkalimetric titration with a standard solution of NaOH, and resulted to be $\geq 99.5\%$. Anhydrous trisodium citrate or citric acid solutions were prepared from the corresponding Fluka or Merck product (puriss. $\geq 99.5\%$) without further purification. Standard NaOH, KOH and HCl solutions were prepared by diluting concentrated Fluka ampoules and standardized against potassium hydrogenphthalate (Fluka, puriss.) and sodium carbonate (Fluka, puriss.), respectively. NaCl and KNO_3 (Fluka, puriss.) were used after stove drying at 140 °C. All solutions were prepared using grade A glassware and ultrapure water (conductivity < 0.1 μS).

2.2 e.m.f. measurements

Potentiometric measurements were performed using apparatus consisting of a Metrohm (mod. E654) potentiometer

equipped with an Orion (Ross mod. 8101) glass electrode coupled with a standard calomel electrode, and a similarly equipped Crison micro-pH 2002 potentiometer; the measurements were made using two different sets of apparatus in order to minimize systematic errors. Instrumental resolution was 0.1 mV. The whole system was controlled by a suitable computer program, which read and saved e.m.f. values when the equilibrium was reached as well as managing titrant delivery, data acquisition and e.m.f. stability checks. Pre-established volumes of titrant were delivered to the measurement cell by an automatic Metrohm Dosimat (mod. 665) burette (minimum reading of 0.001 mL). The experiments were carried out in aqueous solutions containing NaCl as supporting electrolyte at different ionic strength values ($0.1 \leq I/\text{mol L}^{-1} \leq 1.0$); some experiments were also carried out without any addition of supporting electrolyte to the aqueous solutions and where the component concentrations was very low in order to maintain the total ionic strength less than 10 mmol L^{-1} . All the measurements were performed at $t = 25 \pm 0.1$ °C in titration cells equipped with an outer chamber that allows a continue liquid circulation by means of a thermocryostat.

Owing to the complexity of the uranyl-citrate system, the measurements were projected in order to extend the investigations to a wide range of citrate/uranyl molar ratios (from 0.5 : 1 to 6 : 1) using different procedures; in the first one, solutions containing different concentrations of uranyl ion ($0.5 \leq C_{\text{UO}_2^{2+}}/\text{mmol L}^{-1} \leq 20$), citrate ($2.5 \leq C_{\text{cit}}/\text{mmol L}^{-1} \leq 50$) and NaCl (in order to obtain the pre-established ionic strength values) were titrated with standard carbonate-free NaOH solutions until precipitation occurred ($C_{\text{UO}_2^{2+}}$ and C_{cit} refer to the total concentration of the metal and ligand in the measurement cell, respectively); in the second, solutions containing only uranyl ($2.5 \leq C_{\text{UO}_2^{2+}}/\text{mmol L}^{-1} \leq 20$) ion and NaCl were titrated with standard solutions of trisodium citrate salt or trisodium citrate salt and sodium hydroxide. The potentiometric measurements were made by collecting the experimental data in two different ways; firstly, we collected a higher number of experimental points (max. 200 points, measurements [A]), and secondly, we carried out measurements where a relatively small number of experimental points were collected (about 30–50, measurements [B]), but over a longer analysis time (up to 4 h) and applying high average waiting times between two titrant additions (up to 10 min). As an example, in Table 1, we report the experimental conditions used for the measurements at $I = 1.0 \text{ mol L}^{-1}$; the same procedure and experimental conditions were used for the investigation carried out at ionic strength 0.1, 0.25, 0.50 and 0.75 mol L^{-1} in NaCl_{aq} . Table 2 reports the experimental condition used in KNO_3_{aq} 0.1 mol L^{-1} at $t = 25 \pm 0.1$ °C; these measurements were performed by a Metrohm 713 potentiometer (resolution of ± 0.1 mV) equipped with combined glass electrode. The titrant (KOH) was dispensed by a 765 Dosimat (minimum volume deliverable of ± 0.001 mL) automatic burette by Metrohm. During these experiments, the ionic strength was kept constant by using titrand solutions at the same ionic strength (with NaCl or KNO_3) of the solutions under study. For the solutions without addition of supporting electrolyte, where very low component concentrations ($C_{\text{UO}_2^{2+}} < 1 \text{ mmol L}^{-1}$

Table 1. Experimental conditions for the UO_2^{2+} -citrate system in 1 mol L^{-1} NaCl aqueous solution.

Run	Vessel		Titrant			Measurements					
	$C_{\text{UO}_2^a}$	C_{cit}^a	C_{H}^a	C_{cit}^a	$C_{\text{H}}^{a,b}$	n^c	ΔpH^d	n^c	ΔpH^e	m^f	\bar{I}^g
1	0.01497	0.01986	0.05959	0.00000	-1.00010	122	1.93-6.03	40	1.90-6.08	3	1.01
2	0.01497	0.02999	0.08999	0.00000	-1.00010	113	1.88-6.10	42	1.84-9.92	3	1.01
3	0.01497	0.05027	0.15081	0.00000	-1.00010	128	1.84-6.21	46	1.78-9.94	4	1.02
4	0.00499	0.00770	0.02311	0.00000	-1.00010	91	2.21-5.92	30	2.20-5.73	3	0.99
5	0.00499	0.01499	0.04499	0.00000	-1.00010	96	2.12-6.02	34	2.11-10.99	3	1.00
6	0.00499	0.03008	0.09023	0.00000	-1.00010	101	2.02-6.29	45	1.99-6.31	4	1.02
7	0.00499	0.01484	0.04453	0.00000	-1.00010	40	2.13-6.02	35	2.11-9.82	3	1.00
8	0.00250	0.00000	0.00301	0.16700	0.00000	199	2.52-5.67	36	2.51-5.68	4	0.99
9	0.00493	0.00000	0.00301	0.16700	0.00000	199	2.48-5.46	35	2.50-5.37	4	0.99
10	0.00999	0.00000	0.00301	0.16700	0.00000	199	2.51-5.41	42	2.51-5.39	3	0.98
11	0.02007	0.00000	0.00301	0.16700	0.00000	199	2.49-5.36	50	2.52-5.38	4	0.98
12	0.01475	0.03000	0.09001	0.00000	-0.50050	111	1.88-6.05	41	1.85-10.49	3	1.01
13	0.00491	0.03000	0.09001	0.00000	-0.50050	102	2.03-6.27	37	2.00-11.23	3	1.01
14	0.00099	0.00100	0.00705	0.00000	-0.04594	73	2.37-5.17	32	2.30-5.90	3	0.99
15	0.00096	0.00147	0.00835	0.00000	-0.04594	79	2.36-5.47	36	2.30-6.00	4	0.98
16	0.00201	0.00255	0.01170	0.00000	-0.04594	76	2.29-5.06	30	2.25-5.80	3	1.01
17	0.00760	0.00250	0.00750	0.00000	-0.50050	49	2.38-3.84			2	1.00
18	0.00829	0.00824	0.02520	0.00000	-0.50050	45	2.16-5.96			2	1.00
19	0.00704	0.00397	0.01482	0.00000	-0.49050	105	2.19-5.42			1	0.98
20	0.01032	0.00595	0.02084	0.00000	-0.49050	103	2.13-5.61			1	0.97
21	0.00804	0.00501	0.01802	0.00000	-0.49050	109	2.14-6.24			1	0.98
22	0.01009	0.00609	0.02232	0.00000	-0.49050	110	2.06-5.47			1	0.97
23	0.00155	0.00204	0.01017	0.00000	-0.45940	82	2.30-5.45			1	0.98
24	0.00201	0.00256	0.01170	0.00000	-0.45940	76	2.28-5.13			1	0.97
25	0.00896	0.00501	0.01802	0.00000	-0.45940	87	2.13-5.60			1	0.97
26	0.00692	0.00406	0.01625	0.00000	-0.45940	104	2.16-5.50			1	0.97
27	0.00791	0.00508	0.01927	0.00000	-0.48510	107	2.12-5.50			1	0.97
28	0.00910	0.00508	0.01927	0.00000	-0.48510	92	2.11-5.10			1	0.97

a: mol L^{-1} ; b: $-C_{\text{H}} \equiv C_{\text{OH}}$; c: Number experimental points collected; d: Measurements [A]; e: Measurements [B]; f: Number of measurements; g: Mean ionic strength values.

Table 2. Experimental conditions used in the studies of the UO_2^{2+} -citrate system in 0.1 mol L^{-1} KNO_3 aqueous solution.

Run	Vessel		Titrant			Measurements		
	$C_{\text{UO}_2^a}$	C_{cit}^a	C_{H}^a	C_{cit}^a	$C_{\text{H}}^{a,b}$	n^c	ΔpH^d	\bar{I}^e
1	0.00500	0.00500	0.01500	0.00000	-0.50000	33	2.30-6.96	0.117
2	0.00400	0.04000	0.01200	0.00000	-0.50000	34	2.48-6.82	0.113
3	0.00900	0.03080	0.09240	0.00000	-0.50000	19	2.35-4.13	0.112
4	0.00760	0.00250	0.07500	0.00000	-0.50000	19	2.42-4.07	0.110
5	0.00800	0.08180	0.02454	0.00000	-0.50000	16	2.17-3.55	0.115
6	0.00829	0.08240	0.02520	0.00000	-0.50000	35	2.15-6.08	0.122
7	0.00600	0.00612	0.01837	0.00000	-0.50000	25	2.29-6.01	0.116

a: mol L^{-1} ; b: $-C_{\text{H}} \equiv C_{\text{OH}}$; c: Number experimental points collected; d: pH range used for calculations; e: Mean ionic strength values.

and $C_{\text{cit}} < 2 \text{ mmol L}^{-1}$) were used, the lowering of the ionic strength value due to the dilution during the titration is compensated by its increases due to the dissociation of the ligand.

For each experiment, independent titrations of standard HCl solution with standard carbonate free base (NaOH or KOH) were carried out under the same ionic strength conditions as the systems to be investigated, with the aim of determining electrode potential (E^0) and the acidic junction potential ($E_j = j_a[\text{H}^+]$). In this way, the pH scale used was $\text{pH} \equiv -\log[\text{H}^+]$, where $[\text{H}^+]$ is the free proton concentration (not activity). Ionic strength and ionic medium of the calibrating solutions were the same as the solutions being

examined. In each phase of the studies, recommended procedures for potentiometric measurements [47] were adopted and the equilibrium state during titrations was checked by adopting some usual precautions [47]; these included checking the time required to reach equilibrium and performing some back titrations.

In Fig. 1, we report a comparison between a potentiometric titration curve of H_3Cit ($C_{\text{Cit}} = 14.84 \text{ mmol L}^{-1}$ and total $\text{H}^+ = 44.53 \text{ mmol L}^{-1}$) and of a UO_2/Cit solution (run 7 of Table 1) at $I = 1.0 \text{ mol L}^{-1}$ in NaCl aqueous solution; these curves are very important since, they highlight the shift of the titration curve of H_3Cit with respect to the uranyl/citrate ones, due to the complexation.

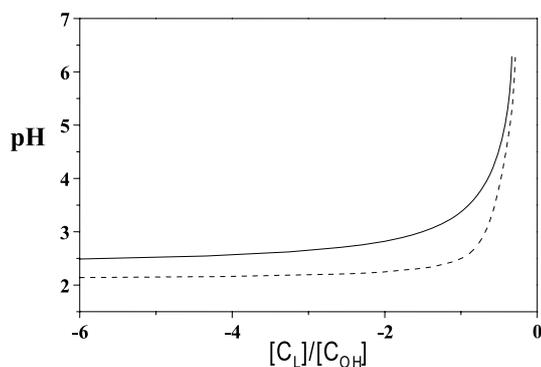


Fig. 1. Titration curves for H_3Cit and $\text{UO}_2\text{-Cit}$ system in NaCl aqueous solution 1.0 mol L^{-1} and $t = 25^\circ\text{C}$. Experimental conditions: — H_3Cit : $C_{\text{Cit}} = 14.84 \text{ mmol L}^{-1}$; $C_{\text{H}^+} = 44.53 \text{ mmol L}^{-1}$; --- UO_2Cit : $C_{\text{UO}_2^{2+}} = 4.99 \text{ mmol L}^{-1}$; $C_{\text{Cit}} = 14.84 \text{ mmol L}^{-1}$; $C_{\text{H}^+} = 44.52 \text{ mmol L}^{-1}$.

2.3 Spectrophotometric measurements

The visible spectrophotometric determinations were carried out with a Jasco V-550 UV/Vis spectrophotometer from 380 to 550 nm (optical path length 1.000 cm).

The solution used for the potentiometric titrations in KNO_3 aqueous solutions, were transferred from the potentiometric to an optical cell using a peristaltic pump in order to record spectra as a function of the pH value of the solution examined. This procedure allowed us to strongly reduce discrepancies between pH-metric and spectroscopic conditions of measurements.

Fig. 2 reports the spectrophotometric titration curve of a solution containing: $C_{\text{UO}_2} = 4 \text{ mmol L}^{-1}$ and $C_{\text{Cit}} = 4 \text{ mmol L}^{-1}$ in KNO_3 0.1 mol L^{-1} , titrated with KOH $0.5000 \text{ mmol L}^{-1}$ in the wavelength interval $\lambda = 380\text{--}550 \text{ nm}$; as can be seen a little bathochromic effect can be observed along the titration.

2.4 Data analysis and calculations

Different computer programs were used for the treatment of the experimental data; in particular the non linear least

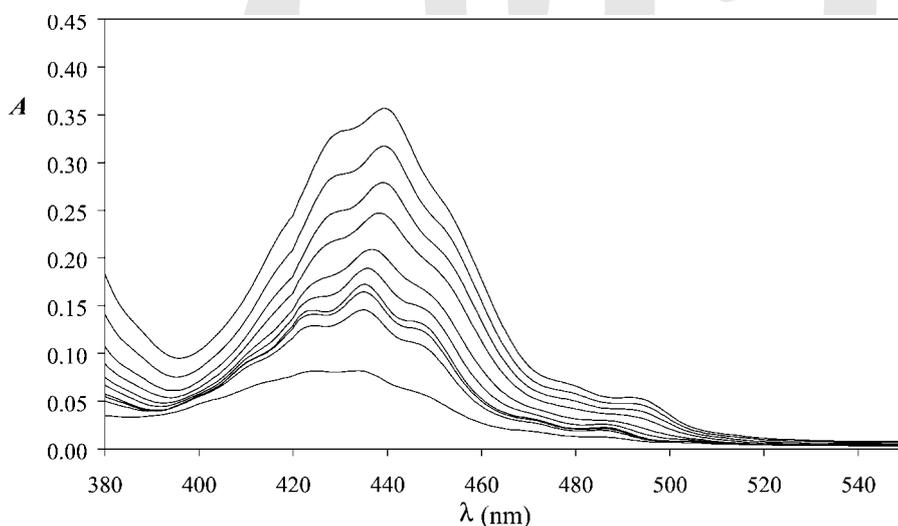
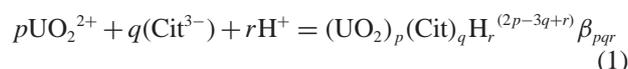


Fig. 2. Spectrophotometric titration curves of the $\text{UO}_2\text{-Cit}$ system in KNO_3 0.1 mol L^{-1} and $t = 25^\circ\text{C}$. Experimental condition: $C_{\text{UO}_2^{2+}} = 4 \text{ mmol L}^{-1}$; $C_{\text{Cit}} = 4 \text{ mmol L}^{-1}$; $C_{\text{H}^+} = 12 \text{ mmol L}^{-1}$.

squares computer program ESAB2M [48] allows to determine all the parameters of an acid–base titration (analytical concentration of reagents, formal electrode potential E^0 , coefficient j_a relative to junction potential – according to the equation: $E_j = j_a [\text{H}^+]$ – and the ionic product of water K_w). The formation constant calculated from potentiometric data were refined by the computer program BSTAC [49] which minimize the error squares sum on electromotive force values. In all the least squares calculations weights were obtained from variance propagation (measurements [A] carried out in NaCl aqueous solutions and at low ionic strength without supporting electrolyte and measurements in KNO_3 aqueous solutions) or from the variance in different experiments (measurements [B] carried out in NaCl aqueous solutions). The ES4ECI [50] program was used to draw distribution diagrams and to calculate the formation percentages of species.

All the formation constants are expressed according to the equilibrium:



with reference to the above equation, both the formulas $(\text{UO}_2)_p(\text{Cit})_q\text{H}_{-r}$ and $(\text{UO}_2)_p(\text{Cit})_q(\text{OH})_r$ in this paper are equivalent and represent the same complex, which very probably is formed by deprotonation of alcoholic hydroxyl of citrate.

The potentiometric data obtained from the measurements at low ionic strength and without addition of supporting electrolyte, can be used to calculate stability constants by extrapolation to infinite dilution.

The $\log \beta_{pqr}$ values at $I = 0 \text{ mol L}^{-1}$ were calculated from potentiometric data in NaCl data using a simple Debye–Hückel type equation for extrapolation purposes [51]:

$$\log \beta_{pqr} = \log \beta_{pqr}^0 - z^* \frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} + CI \quad (2)$$

where β_{pqr}^0 = formation constant at infinite dilution; $z^* = \sum z_{\text{reactants}}^2 - \sum z_{\text{products}}^2$; A = Debye–Hückel constant = 0.51

at $t = 25^\circ\text{C}$, whilst

$$C = c_0 p^* + c_1 z^* \quad (3)$$

(with $p^* = \sum p_{\text{reactants}} - \sum p_{\text{products}}$; z and p are the charge and the stoichiometric coefficient, respectively) is the only adjustable parameter for the dependence of formation constants on ionic strength. Taking into account this approach, it is possible to use a simple equation for the ionic strength dependence of the formation constants, independent of the reactants, and dependent on the type of formation reaction only. Often, this simple choice is sufficient to explain experimental data in a wide ionic strength range, generally $< 3 \text{ mol L}^{-1}$, when the supporting electrolyte is a 1 : 1 alkali metal salt.

Eq. (2) can be used with both the molar and molal concentration scales. Moreover, if the molal concentration scale is used, Eq. (2) is equivalent to the one used for SIT (specific ion interaction theory) [52, 53] with $C \equiv \Delta\varepsilon$ ($\varepsilon =$ specific interaction parameter).

The general least squares computer program LIANA [50] was used for the refinement of $\log \beta_{pqr}^0$ and of the C and ε parameters for the dependence of equilibrium constants on ionic strength. In the first case, Eq. (2) was used, whilst in the second case (Eq. 4) we used the SIT approach (for more details see Sect. 3.5), which can be expressed by the following equation:

$$\log \beta_{pqr} = \log \beta_{pqr}^0 - z^* \frac{A\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} + \Delta\varepsilon I_m + j \log a_w \quad (4)$$

where $I_m =$ ionic strength in the molal concentration scale, $\log a_w$ is the activity coefficient of water ($\log a_w = 0.015$), $j =$ number of water molecules involved in the equilibrium.

Spectrophotometric data were analyzed by means of the HYPERQUAD software [54], which allows to calculate the values of the molar absorption (ε_λ) by using experimental spectra (absorbance, A , versus wavelength, λ/nm), analytical concentrations of the reagents and the chemical model (stoichiometric coefficients and stability constant values of all complexes) as input. After the calculation of the species distribution, the spectra are estimated (deconvolution procedure) for each complex formed in solution (molar absorptivity, $\varepsilon/\text{mol}^{-1} \text{ L cm}^{-1}$, versus wavelength, λ/nm), only assuming the additivity of the absorbance in the investigated concentration range (Lambert–Beer's law). Experimental spectra are then rebuilt starting from the calculated ones (using the concentrations by the species distribution) and a statistical comparison gives rise to the uncertainty evaluation at each wavelength. No assumptions on the shape of the curves nor on the nature of electronic transitions are taken into account by the program.

With the carboxylic ligand here considered we found again the trend previously observed for hydrolysis: the coordination environment produces a little bathochromic shift in the position of λ_{max} . The little shift of λ_{max} does not surprise, since electronic configuration of uranyl makes little significant the action of the ligand field due to the ligand donor atoms and the electronic structure of the complex is essentially determined by the triatomic UO_2^{2+} entity [55].

3. Results and discussion

3.1 Hydrolysis of dioxouranium(VI) and protonation of citrate

The acid–base properties of dioxouranium ion were already widely investigated from our groups in different supporting electrolytes; data in chloride and nitrate aqueous solution were reported in a previous contribution [56]. We observed that the nature of the supporting electrolyte influences the speciation of the metal ion and that the values of the hydrolytic constants are sensible to the change of the ionic strength. For example, in NaCl aqueous solution, we observed the formation of several species, namely: the mononuclear species UO_2OH^+ , generally formed at low uranyl concentrations; the binuclear species $(\text{UO}_2)_2(\text{OH})_2^{2+}$; the trinuclear species $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_3(\text{OH})_7^-$ and the $(\text{UO}_2)_3(\text{OH})_4^{2+}$ species stabilized in chloride media by the formation of a fairly stable ion pair $(\text{UO}_2)_3(\text{OH})_4\text{Cl}^+$ [56]. Instead, in aqueous solutions containing nitrate as counterion, the speciation model is quite simple with respect to NaCl; in fact at low metal concentration, the acid–base properties of UO_2^{2+} can be modelled taking into account only the $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^+$ species. For the formation constants relative to hydrolysis reactions and the visible absorption spectra referred to uranyl ion and single hydrolytic species, our previous values [57] have been employed.

Independently of the ionic medium used, the hydrolytic species of uranyl generally reach high formation percentages at $\text{pH} \geq 3.5$ even in the presence of O-donor ligands, and consequently, they cannot be neglected in an accurate speciation model of natural waters and biological fluids. Table 3 reports the hydrolytic constants of dioxouranium(VI) [56] at different ionic strengths in the molar concentration scale; SIT parameters were already calculated in NaCl aqueous solution [56]. Table 3 reports also the hydrolytic constants in KNO_3 and $I = 0.1 \text{ mol L}^{-1}$, at $t = 25^\circ\text{C}$ for the $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^+$ species.

As regards the acid–base properties of citric acid, these were largely investigated in the past; recently a last compilation of selected stability constants is found in the literature [58]. Nevertheless for the work of this paper, we carried out new experiments in NaCl aqueous solutions

Table 3. Equilibrium constants for the hydrolysis of dioxouranium(VI) in NaCl_{aq} and KNO_3 at $t = 25^\circ\text{C}$.

p	q	$I = 0^a$	$I = 0.1^a$	$I = 0.5^a$	$I = 1.0^a$
				$-\log \beta_{pq}^c$	
				NaCl ^b	
1	1	5.19	5.45	5.72	5.96
2	2	5.76	5.98	6.14	6.24
3	4	11.82	12.22	12.38	12.41
3	5	15.89	16.55	16.93	17.13
3	7	29.26	29.68	29.79	29.80
				KNO ₃ ^b	
2	2		5.90		
3	5		16.35		

a: mol L^{-1} ; b: Ref. [56]; c: $\log \beta_{pq}$ refers to the equilibrium: $p\text{UO}_2^{2+} + q\text{H}_2\text{O} = (\text{UO}_2)_p(\text{OH})_q^{(2p-q)} + q\text{H}^+$.

Table 4. Protonation constants of citric acid in both molar and molal concentration scale in NaCl_{aq} and $t = 25\text{ }^\circ\text{C}$.

$I/\text{mol L}^{-1}$	$\log K_1^H$	$\log K_2^H$	$\log K_3^H$
0.099	5.775 ± 0.009^a	4.353 ± 0.010	2.923 ± 0.010
0.494	5.417 ± 0.005	4.142 ± 0.006	2.822 ± 0.006
0.978	5.284 ± 0.005	4.088 ± 0.006	2.803 ± 0.006
1.920	5.208 ± 0.005	4.111 ± 0.005	2.836 ± 0.006
2.823	5.215 ± 0.004	4.193 ± 0.006	2.906 ± 0.006
4.516	5.331 ± 0.009	4.441 ± 0.010	3.109 ± 0.010

$I/\text{mol kg}^{-1}$	$\log K_1^H$	$\log K_2^H$	$\log K_3^H$
0.1	5.773	4.351	2.921
0.5	5.412	4.137	2.817
1.0	5.275	4.079	2.794
2.0	5.190	4.093	2.818
3.0	5.189	4.167	2.880
5.0	5.287	4.397	3.065

a: \pm std. dev.

($0.1 \leq I/\text{mol L}^{-1} \leq 1.0$ and $t = 25\text{ }^\circ\text{C}$), and the experimental protonation constants obtained were elaborated all together with literature values, in order to propose recommended protonation constants in this very important supporting electrolyte. The obtained protonation constants reported in Table 4, are in good agreement with the selected ones evaluated in Refs. [28] and [58]. The parameters for the dependence of the protonation constants of citric acid on ionic strength were calculated by means of the simple Debye–Hückel (Eq. 2) and SIT (Eq. 4) equations (Table 5). Instead, for the KNO₃ ionic medium, literature values were used [58].

Table 5. Parameters for the dependence on ionic strength of the protonation constants of citrate in NaCl_{aq} and $t = 25\text{ }^\circ\text{C}$.

p	r	$\log \beta_{pr}^0$ ^a	C^b	SIT parameters
1	1	6.397 ± 0.010^c	0.098 ± 0.005	$\varepsilon[\text{L}^{3-}, \text{Na}^+] = 0.133 \pm 0.004$
1	2	11.159 ± 0.011	0.151 ± 0.06	$\varepsilon[\text{HL}^{2-}, \text{Na}^+] = 0.151 \pm 0.003$
1	3	14.288 ± 0.011	0.107 ± 0.06	$\varepsilon[\text{H}_2\text{L}^-, \text{Na}^+] = 0.127 \pm 0.003$
				$k_m = 0.150^d$

a: Protonation constant at infinite dilution in molar concentration scale (mol L^{-1}); b: parameter for the dependence of protonation constants on ionic strength (Eq. (2)); c: \pm std. dev.; d: estimated value of the neutral species (H_3L^0).

Table 6. Overall formation constants (molar concentration scale) for some proposed speciation models and comparison with the accepted one for the UO₂²⁺-citrate system in NaCl_{aq} at $I = 0.1\text{ mol L}^{-1}$ and $t = 25\text{ }^\circ\text{C}$.

UO ₂ (Cit) ⁻	(UO ₂) ₂ (Cit) ₂ ²⁻	(UO ₂) ₂ (Cit) ₂ (OH) ₂ ⁴⁻	(UO ₂) ₂ (Cit) ₂ (OH) ₃ ³⁻	(UO ₂) ₂ (Cit)(OH) ₂ ⁻	(UO ₂) ₂ (Cit)(OH) ⁰	(UO ₂) ₃ (Cit) ₂ (OH) ₅ ⁵⁻	σ^2/σ_0^2
7.51 ± 0.05^a	19.50 ± 0.01^a	8.22 ± 0.02^a	14.02 ± 0.02^a	4.031 ± 0.03^a	8.02 ± 0.03^a	-2.03 ± 0.06^a	1.000 ^b
7.54 ± 0.06	19.57 ± 0.01	8.36 ± 0.02	13.99 ± 0.02	3.84 ± 0.04	–	-2.42 ± 0.07	1.48
7.58 ± 0.04	19.42 ± 0.01	8.45 ± 0.01	14.22 ± 0.01	–	–	-2.78 ± 0.04	1.06
8.07 ± 0.04	19.18 ± 0.01	8.26 ± 0.07	–	–	8.38 ± 0.03	-1.77 ± 0.07	1.73
7.91 ± 0.04	19.31 ± 0.02	8.19 ± 0.07	–	3.89 ± 0.09	7.74 ± 0.03	-2.39 ± 0.07	1.47
7.41 ± 0.02	–	–	–	2.19 ± 0.02	6.96 ± 0.02	–	3.27
8.13 ± 0.091	–	–	–	3.47 ± 0.02	7.79 ± 0.03	-2.19 ± 0.04	1.92
7.81 ± 0.10	18.89 ± 0.01	–	–	3.90 ± 0.01	8.11 ± 0.02	-2.44 ± 0.05	1.87
8.00 ± 0.04	18.84 ± 0.01	–	–	–	8.48 ± 0.02	-1.75 ± 0.07	2.08

a: \pm std. dev.; b: $\sigma_0 = 1.357$.

3.2 Speciation model for the dioxouranium(VI) – citrate system

In order to obtain the simplest speciation model, the stability constants of a variety of species were refined alternately with the BSTAC program. The experimental data obtained at each ionic strength value were processed separately, and in Table 6, we report as an example, a comparison between some speciation models checked and the proposed one for the measurements carried out at $I = 0.1\text{ mol L}^{-1}$; the same procedure was used for the other ionic strengths, with similar results.

In Table 6, we also report the results of a statistical analysis of the values obtained from the different speciation models tested and the values of corresponding ratios between single variances in comparison with those from the accepted model (see Table 6, last column). The high number of measurements made and of degree of freedom allowed us to consider to be significant, at 95% confidence interval, even the very low differences in variance between the accepted model and other models.

As already reported in the experimental section, different procedures were employed in our speciation studies on the dioxouranium(VI)-citrate system. Measurements were carried out in experimental conditions (see Table 1) covering a wide range of reagent concentrations, ligand/metal molar ratios and pH, in order to make it possible to find a reliable speciation model.

Initially, on the basis of some literature data [20, 28], we checked the possibility of formation of some simple mononuclear species, such as UO₂(Cit)⁻, UO₂(Cit)H⁰ and UO₂(Cit)H₂⁺ (acid pH range) and of the UO₂(Cit)(OH)²⁻

(basic pH range). Among them only the $\text{UO}_2(\text{Cit})^-$ was satisfactorily refined by our computer program independently of the speciation model, whilst the protonated species and the ternary hydrolytic species were sometime rejected or their formation percentage was lower than 4% (minor species) and then neglected. This can be justified taking into account that our measurements were carried out in the pH range 2.5–7.0, and probably these protonated and hydrolytic uranyl species form outside this range.

From the literature it is well known that citric acid tends to form with metals, and actinides in particular, polynuclear species having high stability, and since relatively high component concentrations used in our investigations, we checked the formation of binary and trinuclear species. First of all, our check was the determination of the stability constants of the $(\text{UO}_2)_2(\text{Cit})_2^{2-}$, which is the most stable uranyl/citrate species [8, 9, 11, 14, 15, 19, 28, 36] and that reaches, also at low component concentrations ($C_{\text{UO}_2^{2+}} > 1 \text{ mmol L}^{-1}$), high formation percentage (more than 80%). Since measurement were carried out up to the basic pH range, we checked and observed the formation, of two binuclear hydrolytic species, namely $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$ and $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{3-}$, formed at $\text{pH} \geq 4.5$ with high formation percentage. Taking into account these species, we observed a significant improvement of the statistical parameters (*i.e.* mean deviation, standard deviation, refined proton concentrations), as it can be seen from the values reported in Table 6. Successively, since some measurements were carried out in large excess of uranyl with respect to citrate (see for example runs 17–22, 25–28 of Table 1), we hypothesized the formation of other ternary species in which the stoichiometric coefficient of the metal ion was in excess with respect to the ligand. The best results were obtained taking into account for the new speciation model, the $(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$ and $(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$ species, respectively. These species form in quite different pH ranges; in particular the formation of the $(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$ neutral species begins at pH 2.5 and reaches its maximum formation percentage at pH 4, whilst for the $(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$, the maximum formation percentage was obtained at pH 5. Some other uranyl trinuclear species were checked, but only the $(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$ allowed us to obtain a significant improvement of the statistical parameters; moreover for measurements carried out with a large excess of metal ion, with respect to citrate, this species reaches formation percentage higher than 80% (run 19–22, 25–29 of Table 1).

Owing to the complexity of the investigated system, the criteria used to select the chemical model are: a) the agreement between results of the dataset [A] and [B] when refined separately; b) the value of the variance ratio; c) the simplicity of the model (other minor species can be added to the chosen ones but the model becomes unrealistically complicated); d) the likelihood of the proposed species, in particular in relation to formation percentage obtained in the different trials.

Despite the speciation model proposed appears complicated for the numerous species included, none of them can be neglected since each of them reaches significant yields in different experimental conditions. As an example, Table 7 shows the maximum formation percentage and the corresponding pH value for each species in some ex-

Table 7. Maximum formation percentage and corresponding pH values for each species in UO_2^{2+} -citrate system at $I = 1.0 \text{ mol L}^{-1}$ and $t = 25^\circ \text{C}$ in NaCl aqueous solution.

Species	% max	pH	Run	R^a
$\text{UO}_2(\text{Cit})^-$	27.8	3.0	6	6.02
	36.4	3.5	16	1.27
	40.2	3.5	23	1.31
	59.5	3.5	7	2.97
$(\text{UO}_2)_2(\text{Cit})_2^{2-}$	79.7	3.1	1	1.33
	80.0	2.9	12	2.03
	80.6	2.9	2	2.00
	81.0	2.8	3	3.36
$(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$	58.3	5.6	5	3.08
	64.8	5.7	3	3.36
	65.2	5.7	13	6.02
	65.6	5.7	6	6.10
$(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{3-}$	41.7	4.9	1	1.33
	41.7	5.0	12	2.03
	41.8	4.9	3	3.36
	42.0	4.9	2	2.00
$(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$	50.4	4.5	22	0.60
	52.8	4.6	26	0.59
	55.6	4.5	25	0.56
	55.8	4.5	28	0.56
$(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$	28.4	3.8	26	0.59
	29.7	3.9	22	0.60
	30.9	3.8	25	0.56
	31.0	3.8	28	0.56
$(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$	84.8	6.5	2	2.00
	87.7	5.5	27	0.64
	89.0	6.5	1	1.33
	92.8	6.2	21	0.62

$$R = [\text{ligand}]/[\text{metal}].$$

perimental conditions at $I = 1.0 \text{ mol L}^{-1}$. As we can see, the formation percentages are strictly dependent on the concentration, pH and molar ratio of components. In particular at $\text{pH} < 4$, the $\text{UO}_2(\text{Cit})^-$, $(\text{UO}_2)_2(\text{Cit})_2^{2-}$ and the $(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$ species reach their maximum formation percentage. It can be observed for the first two species that they form at low ligand/metal molar ratios (R), and that, in the case of the $\text{UO}_2(\text{Cit})^-$ species, its formation reduces significantly for R values greater than ~ 6 . On the contrary for R values from 1 to ~ 4 , the formation percentage of the $\text{UO}_2(\text{Cit})^-$ undergoes low variation. The $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{3-}$ and $(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$ species are formed in high amounts in the pH range from 4 to 5, but at different ligand/metal molar ratios. From the values reported in Table 7, we observed that the formation percentages of the $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{3-}$ species seem to be independent of the ligand/metal molar ratios for the measurements where the ligand was in excess with respect to the metal.

The ultimate criteria that allowed us to consider the robustness of the proposed speciation model is that it was obtained at each ionic strength investigated in NaCl aqueous solutions.

Further validation of the results obtained in NaCl aqueous solution is that similar speciation model was obtained from the investigation carried out in KNO_3 aqueous solution at $I = 0.1 \text{ mol L}^{-1}$.

Table 8. Comparison between the stability constants of the uranyl-citrate species in the two ionic media at $I = 0.1 \text{ mol L}^{-1}$ at $t = 25 \text{ }^\circ\text{C}$.

$I/\text{mol L}^{-1}$	$\text{UO}_2(\text{Cit})^-$	$(\text{UO}_2)_2(\text{Cit})_2^{2-}$	$(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$	$(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{3-}$	$(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$	$(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$	$(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$
0.1	7.51 ± 0.05	19.50 ± 0.01	8.22 ± 0.02	14.02 ± 0.02	4.031 ± 0.03	8.02 ± 0.03	-2.03 ± 0.06
				NaCl			
0.1	7.84 ± 0.05	19.26 ± 0.02	8.87 ± 0.01	14.05 ± 0.03	3.62 ± 0.06	7.88 ± 0.03	-0.92 ± 0.03
				KNO ₃			

It is important to point out that independently of the ionic media used, we observed that the formation of the hydrolytic species of uranyl was inhibited by the presence of citrate; this factor is very important in the environmental problems, where it is essential to limit the amount and mobility of the free metals in the natural systems, and this probably justify the similarity of the speciation model in the two ionic media.

3.3 Stability constants of the uranyl-citrate system

On the basis of previous papers [57, 59–64] and of the considerations on the speciation model above reported, in Table 8 we report as an example a comparison between the stability constants obtained from potentiometric titrations, for the uranyl-citrate system both in NaCl and KNO₃ aqueous solution at 0.1 mol L^{-1} and $t = 25 \text{ }^\circ\text{C}$.

In some cases, especially for the most negatively charged $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$ and $(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$ species, the stability constants in KNO₃ aqueous solution appear significantly higher; this difference can be justified taking into account the influence and the stabilizing effect of the different ions of the supporting electrolytes used. In order to point out the effect of the supporting electrolytes on the acid–base properties of the metal ion, it is sufficient to observe the different speciation models for the hydrolysis of uranyl (see Table 3), and the corresponding hydrolytic stability constants in the two ionic media.

Experimental data at $I = 0.1 \text{ mol L}^{-1}$ in KNO₃ aqueous solutions, obtained both from potentiometric and spectrophotometric data, were processed separately by different computer programs.

By using spectrophotometric data, the formation constants were calculated by HYPERQUAD software [54]. The molar absorptivity coefficients of the uranyl aquaion and of the $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^{5+}$ species, considered in the input, were kept constant during the calculation. From the elaboration of spectrophotometric data we determined the stability constants only of the $(\text{UO}_2)_2(\text{Cit})_2^{2-}$, $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{3-}$, $(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$ and $(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$. The stability constants obtained at $I = 0.1 \text{ mol L}^{-1}$ are: 18.97 ± 0.12 , 14.03 ± 0.11 , 8.14 ± 0.22 and 3.87 ± 0.13 , respectively. The stability constants of the other uranyl-citrate species, namely $(\text{UO}_2)(\text{Cit})^-$, $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$ and $(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$, were those calculated from potentiometric data and were kept constant during the elaboration. The difficulty to determine the whole set of seven stability constants of uranyl-citrate species only from spectrophotometric titrations can be due, probably, to the more limited number of experimental points collected for each titration.

As regards the potentiometric measurements in NaCl aqueous solutions, since these were carried out at different ionic strength values, the experimental data were also elaborated all together in order to model the dependence of stability constants on ionic strength and to calculate the values at infinite dilution. To this aim, two approaches were used (see Table 9); in the first one the dependence on ionic strength was studied by means of the Eq. (2), where the dependence of the stability constants on the salt concentration was modelled by means of the single C parameters calculated for each species of the speciation model. Successively, the dependence of the formation constants on ionic strength

Table 9. Thermodynamic formation constants (molar concentration scale) and parameters for their dependence on ionic strength obtained by using different approaches in NaCl_{aq} and $t = 25 \text{ }^\circ\text{C}$.

Species	Model		
	$\log \beta_{pqr}^0$	C	$\log \beta_{pqr}^0$
$\text{UO}_2(\text{Cit})^-$	$9.16 \pm 0.03^{a,b}$	$0.44 \pm 0.05^{a,b}$	$8.81 \pm 0.03^{b,c}$
$(\text{UO}_2)_2(\text{Cit})_2^{2-}$	21.81 ± 0.02	-0.04 ± 0.03	21.87 ± 0.01
$(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$	9.29 ± 0.03	-0.12 ± 0.04	9.08 ± 0.01
$(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{3-}$	16.04 ± 0.04	-0.12 ± 0.05	15.75 ± 0.01
$(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$	5.30 ± 0.011	-0.068 ± 0.14	5.57 ± 0.01
$(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$	9.65 ± 0.07	-0.054 ± 0.09	9.77 ± 0.02
$(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$	-1.53 ± 0.06	0.14 ± 0.07	-2.01 ± 0.01
σ	1.48	–	1.36
M.D.	2.31	–	1.82
c_0	–	–	0.187 ± 0.003
c_1	–	–	-0.031 ± 0.001

Refined parameters for the dependence of formation constants on ionic strength: a: from Eq. (2); b: \pm std. dev.; c: c_0 and c_1 of Eq. (3).

Table 10. Suggested values for the uranyl-citrate species at different ionic strength and $t = 25^\circ\text{C}$.

$I/\text{mol L}^{-1}$	$\text{UO}_2(\text{Cit})^-$	$(\text{UO}_2)_2(\text{Cit})_2^{2-}$	$(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$	$(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_3^{3-}$	$(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$	$(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$	$(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$
0	9.020 ± 0.012^a	21.820 ± 0.013	9.112 ± 0.011	15.779 ± 0.009	5.462 ± 0.012	9.713 ± 0.008	-1.980 ± 0.026
0.1	7.704 ± 0.011	19.414 ± 0.012	8.233 ± 0.010	14.023 ± 0.007	3.907 ± 0.011	7.948 ± 0.007	-1.993 ± 0.023
0.25	7.262 ± 0.012	18.615 ± 0.011	7.936 ± 0.009	13.433 ± 0.006	3.363 ± 0.010	7.344 ± 0.006	-2.013 ± 0.021
0.50	6.901 ± 0.020	17.970 ± 0.013	7.691 ± 0.011	12.950 ± 0.007	2.893 ± 0.009	6.838 ± 0.004	-2.046 ± 0.023
0.75	6.686 ± 0.030	17.594 ± 0.018	7.544 ± 0.015	12.662 ± 0.011	2.594 ± 0.009	6.527 ± 0.002	-2.079 ± 0.031
1	6.533 ± 0.041	17.333 ± 0.024	7.438 ± 0.020	12.458 ± 0.015	2.368 ± 0.011	6.299 ± 0.001	-2.112 ± 0.041
C^b	-0.039 ± 0.036	0.012 ± 0.010	-0.042 ± 0.019	-0.057 ± 0.016	-0.238 ± 0.014	-0.150 ± 0.008	-0.132 ± 0.051

a: \pm std. dev.; b: parameter for the dependence of stability constants on ionic strength (Eq. 2).

was studied by using Eq. (3) and refining the c_0 and c_1 parameters. In this case, the refined parameters did not refer to the single species, but are common parameters for all the uranyl-citrate species. The good agreement between the refined parameters for the dependence of stability constants on ionic strength and the theoretical ones, can be considered a further indication of the validity of the results obtained and of the goodness of the speciation model proposed. The stability constants (both at infinite dilution and at each ionic strength value: $0.1 \leq I/\text{mol L}^{-1} \leq 1.0$) obtained by using these approaches, were used and processed with the Eq. (2), by means of the LIANA computer program in order to calculate suggested stability constants for each species at the different ionic strength values (Table 10).

Figs. 3–5 report some comparisons between the distribution diagrams of the uranyl-citrate system obtained in different experimental conditions. In particular, in Fig. 3 we report a comparison for the distribution of the species at $I = 0.1$ M in NaCl aqueous solution at $C_{\text{UO}_2^{2+}} = 1.5$ mmol L $^{-1}$, but at two different ligand concentrations, namely 1.5 and 3.0 mmol L $^{-1}$, respectively. It can be observed that all the species reach significant formation percentage, and that their corresponding amount is strictly dependent on the component concentration and on the ligand/metal ratio. In fact, it is possible to observe that the formation percentage of the species obtained at $C_{\text{UO}_2^{2+}} = 1.5$ mmol L $^{-1}$ and $C_{\text{Cit}^{3-}} = 3.0$ mmol L $^{-1}$ have higher formation percentage with respect to the corresponding ones obtained for $C_{\text{Cit}^{3-}} = 1.5$ mmol L $^{-1}$,

but for the $(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$, $(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$ and the $(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$ (where the stoichiometric coefficient of UO_2^{2+} is higher with respect to citrate). This indicates that not only the component concentration, but also the ligand/metal ratio, are hauling factor on the speciation of a metal-ligand system. Similarly in Fig. 4 a comparison between the distribution diagrams obtained at $I = 0.1$ mol L $^{-1}$

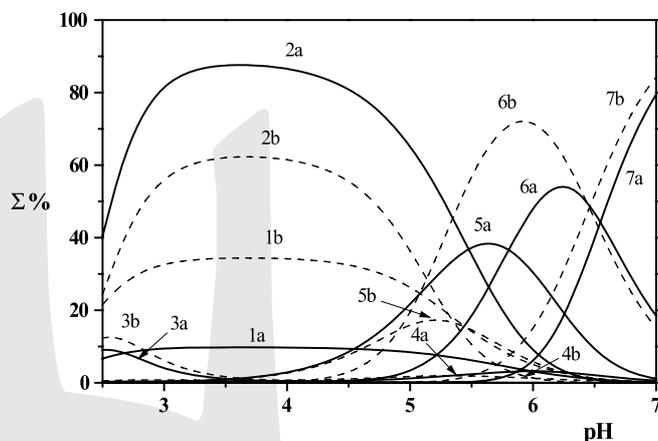


Fig. 4. Distribution diagram of the uranyl-citrate species in NaCl_{aq} and KNO_3_{aq} at $I = 0.1$ mol L $^{-1}$ and $t = 25^\circ\text{C}$. Experimental conditions: $C_{\text{UO}_2^{2+}} = 1.5$ mmol L $^{-1}$, $C_{\text{Cit}^{3-}} = 3.0$ mmol L $^{-1}$. a) NaCl; b) KNO_3 . Species: 1. $\text{UO}_2(\text{Cit})^-$; 2. $(\text{UO}_2)_2(\text{Cit})_2^{2-}$; 3. $(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$; 4. $(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$; 5. $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_3^{3-}$; 6. $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$; 7. $(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$.

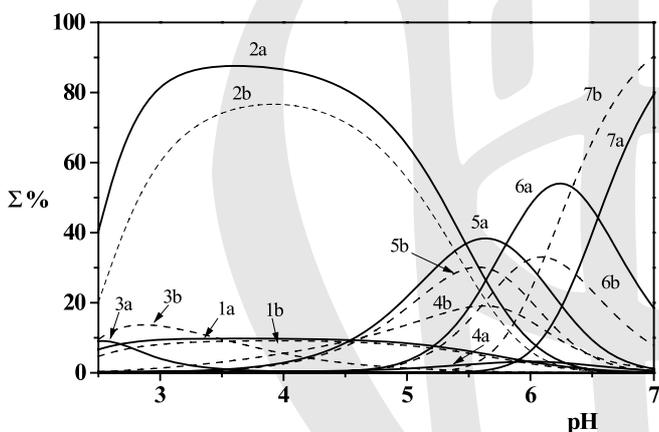


Fig. 3. Distribution diagram of the uranyl-citrate species in NaCl_{aq} 0.1 mol L $^{-1}$ and $t = 25^\circ\text{C}$. Experimental conditions: a) $C_{\text{UO}_2^{2+}} = 1.5$ mmol L $^{-1}$, $C_{\text{Cit}^{3-}} = 3.0$ mmol L $^{-1}$. b) $C_{\text{UO}_2^{2+}} = 1.5$ mmol L $^{-1}$, $C_{\text{Cit}^{3-}} = 1.5$ mmol L $^{-1}$. Species: 1. $\text{UO}_2(\text{Cit})^-$; 2. $(\text{UO}_2)_2(\text{Cit})_2^{2-}$; 3. $(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$; 4. $(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$; 5. $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_3^{3-}$; 6. $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$; 7. $(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$.

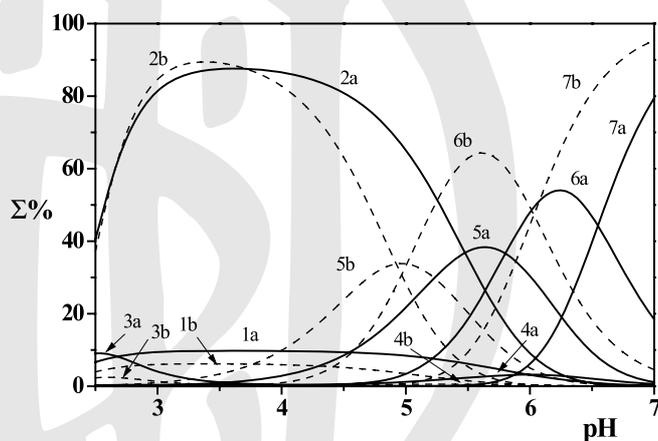


Fig. 5. Distribution diagram of the uranyl-citrate species in NaCl_{aq} at different ionic strength values and $t = 25^\circ\text{C}$. Experimental conditions: $C_{\text{UO}_2^{2+}} = 1.5$ mmol L $^{-1}$, $C_{\text{Cit}^{3-}} = 3.0$ mmol L $^{-1}$. a) $I = 0.1$ mol L $^{-1}$; b) $I = 1.0$ mol L $^{-1}$. Species: 1. $\text{UO}_2(\text{Cit})^-$; 2. $(\text{UO}_2)_2(\text{Cit})_2^{2-}$; 3. $(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$; 4. $(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$; 5. $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_3^{3-}$; 6. $(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$; 7. $(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$.

but in the two ionic media, namely NaCl and KNO₃, is reported; also in this case it can be observed that the experimental conditions and the ionic media play a fundamental role on the distribution of the species. Another evidence is reported in Fig. 5, where the distribution of the species of the uranyl-citrate system is reported at two different ionic strengths, namely 0.1 and 1.0 mol L⁻¹ in NaCl aqueous solution. It is interesting to observe, at $I = 1.0 \text{ mol L}^{-1}$ with respect to 0.1 mol L⁻¹, a significant shift in the maximum of the formation percentage of the species, as well as, a higher formation percentage of the high negatively charged species. This effect can be attributed to the stabilizing effect of the cation of the supporting electrolyte with respect to these species.

3.4 Spectra of uranyl citrate complexes

The individual spectra of the seven uranyl-citrate species were calculated starting from the experimental spectra (see for example Fig. 2) and from the known values of reagent analytical concentrations and of the complex stability constants, as reported in the *Data analysis and calculations* paragraph. The spectra of the different complexes are drawn in Fig. 6 and the values of λ_{max} and ϵ_{max} for each complex are listed in the caption of the same figure. The uncertainty estimated on ϵ_{max} values ranges between 2 and 8% ($\pm 3s$), according to the formation percentage of each single complex reached in solution. With the citric acid we have found that the co-ordination environment produces an increase in the molar absorptivity values (the ϵ_{max} of aquaion is 8 L mol⁻¹ cm⁻¹ [57]) and a bathochromic shift in the position of λ_{max} (the λ_{max} of aquaion is 414 nm [57]). This trend is in accordance with the results previously obtained for hydrolysis and complexes of other carboxylic ligands [57, 64], but the bathochromic shift is greater for citric acid. Comparing the values of ϵ_{max} of citrate complexes, normalized for the chromophores number for each complex, we observe that the trimer (UO₂)₃(Cit)₂(OH)₅⁵⁻ shows a particularly high value with respect to other com-

plexes. This finding confirms previous results obtained about polymeric hydrolytic species [57]: the polymerization and the metal coordination by OH⁻ ion raise ϵ_{max} values and provide a bathochromic shift in the absorption maximum. Meinrath *et al.* [65] showed the same spectroscopic behavior of hydrolytic species of uranyl and wrote that it is yet unclear, whether the shift in the absorption maximum observed is due to changes in the vibronic fine structure or due to a shift in the electronic transition. This spectrophotometric behavior was detected also for not polymeric species. For example, in our previous work [64] reports high values of ϵ_{max} and λ_{max} for the complex UO₂(TODA)(OH)⁻ (TODA = 3,6,9 trioxaundecanedioic acid), and a marked increase in the absorption values and in the red shift was also showed in a work of Moll *et al.* [66] for the uranyl- α -hydroxyisobutyrate system at pH higher than 5. In this region the authors proposed the formation of the complex UO₂[OC(CH₃)₂COO]₂²⁻.

Furthermore the significant difference in ϵ_{max} values calculated for dimeric and trimeric species confirms that UO₂²⁺ tends to polymerize even at low metal concentration in order to form not only dimeric but also trimeric complexes.

3.5 Ionic strength dependence: SIT parameters

According to the SIT (Specific Ion Interaction Theory), for the species X the relative activity coefficients can be expressed as

$$\log \gamma_x = -z_x^2 D + \sum_i \epsilon(X, Y_i) m_i \quad (5)$$

where:

$$D = \frac{A\sqrt{I_m}}{1 + 1.5\sqrt{I_m}},$$

$A = 0.51$ ($t = 25 \text{ }^\circ\text{C}$); I_m = ionic strength in mol kg⁻¹; Y_i = ionic species present in the solution; m_i = concentration in mol kg⁻¹ (H₂O); $\epsilon(X, Y_i)$ = interaction coefficients.

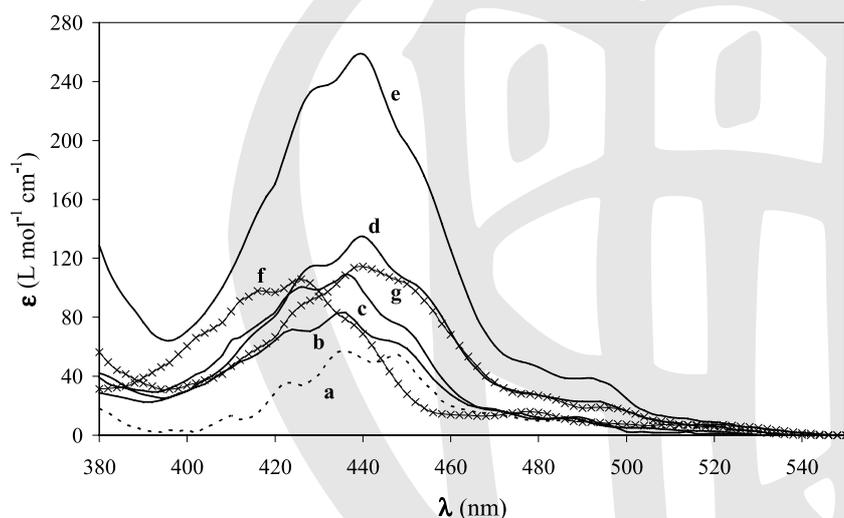


Fig. 6. Molar absorptivities of the uranyl-citrate species at $I = 0.1 \text{ mol L}^{-1}$ in KNO₃ and $t = 25 \text{ }^\circ\text{C}$. Curves: --- line for mononuclear species, a. UO₂(Cit)⁻, $\lambda_{\text{max}}(\epsilon_{\text{max}}) = 436(57)$; — line for polymeric species, b. (UO₂)₂(Cit)₂²⁻, $\lambda_{\text{max}}(\epsilon_{\text{max}}) = 435(83)$, c. (UO₂)₂(Cit)₂(OH)³⁻, $\lambda_{\text{max}}(\epsilon_{\text{max}}) = 436(109)$, d. (UO₂)₂(Cit)₂(OH)₂⁴⁻, $\lambda_{\text{max}}(\epsilon_{\text{max}}) = 440(135)$, e. (UO₂)₃(Cit)₂(OH)₅⁵⁻, $\lambda_{\text{max}}(\epsilon_{\text{max}}) = 440(259)$; × line for binuclear species, f. (UO₂)₂(Cit)(OH)⁰, $\lambda_{\text{max}}(\epsilon_{\text{max}}) = 426(106)$, g. (UO₂)₂(Cit)(OH)₂⁻, $\lambda_{\text{max}}(\epsilon_{\text{max}}) = 441(114)$. The wavelengths (λ_{max}) and the molar absorptivities (ϵ_{max}) of absorption maxima are expressed in nm and L mol⁻¹ cm⁻¹, respectively.

Table 11. Specific interaction coefficients for the uranyl-citrate species in NaCl_{aq} and $t = 25^\circ\text{C}$.

Species	Interaction ^a	ε
$\text{UO}_2(\text{Cit})^-$	$\varepsilon(\text{ML}^-, \text{Na}^+)$	0.418 ± 0.001^b
$(\text{UO}_2)_2(\text{Cit})_2^{2-}$	$\varepsilon(\text{M}_2\text{L}_2^{2-}, \text{Na}^+)$	0.768 ± 0.003
$(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$	$\varepsilon(\text{M}_2\text{L}_2(\text{OH})_2^{4-}, \text{Na}^+)$	0.558 ± 0.001
$(\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{3-}$	$\varepsilon(\text{M}_2\text{L}_2(\text{OH})_2^{3-}, \text{Na}^+)$	0.698 ± 0.002
$(\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$	$\varepsilon(\text{M}_2\text{L}(\text{OH})_2^-, \text{Na}^+)$	0.604 ± 0.001
$(\text{UO}_2)_2(\text{Cit})(\text{OH})^0$	$K_m = (\text{M}_2\text{L}(\text{OH})^0)$	0.649 ± 0.003
$(\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$	$\varepsilon(\text{M}_3\text{L}_2(\text{OH})_5^{5-}, \text{Na}^+)$	0.513 ± 0.003

a: $\text{M} = \text{UO}_2^{2+}$; $\text{L} = \text{Cit}^{3-}$; b: \pm std. dev.

For simple electrolytes, such as HCl , NaCl , Na_2SO_4 , ..., the interaction coefficient can be calculated from the mean molal activity coefficient γ_{\pm} :

$$\gamma_{\pm} = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/\nu}$$

$$\nu \log \gamma_{\pm} = \nu_+ \log \gamma_+ + \nu_- \log \gamma_-$$

(ν_+ and ν_- are the stoichiometric coefficients of the simple electrolyte; $\nu = \nu_+ + \nu_-$). Using Eq. (5), after simple manipulation, one obtain:

$$\log \gamma_{\pm} = -|z_+ z_-| D + (2\nu_+ \nu_- / \nu) \varepsilon(X, Y) m \quad (6)$$

Combining Eqs. (4) and (6), we calculated the specific ionic interaction coefficients for all the protonated species of citrate and of the uranyl-citrate ones; in this last case, the specific interaction coefficients were calculated from the suggested values calculated as already described. These coefficients are reported in Table 11.

When a neutral species is present in the solution, we may use the Setschenow coefficient as interaction coefficient, and in this case the activity coefficient is given by:

$$\log \gamma = k_m I$$

For the SIT calculations in NaCl aqueous solutions, we used for UO_2^{2+} and H^+Cl^- , respectively, the following interaction coefficients: $\varepsilon[\text{UO}_2^{2+}, \text{Cl}^-] = 0.25$ [59], and $\varepsilon[\text{H}^+, \text{Cl}^-] = 0.11$ [59].

Conversion from molar to molal scale in NaCl aqueous solution was obtained using the following procedures reported in Ref. [67].

The dependence on ionic strength of the stability constants of the UO_2^{2+} -Cit complexes, is reported in Fig. 7; in this case we plotted the function $(\log \beta_{pqr} + z^* \text{D.H.})$ vs. $I/(\text{mol kg}^{-1})$. For example, considering the equation $\text{UO}_2^{2+} + \text{Cit}^{3-} = \text{UO}_2\text{Cit}^-$, we have: $(\log \beta_{110} + 12 \text{D.H.})$ vs. $I/\text{mol kg}^{-1}$.

3.6 Sequestering ability of citrate

In the problematic dealing with the environmental pollution of natural systems from metal ions, such as actinides, it is fundamental to have a parameter that allows to estimate the capacity of one or more ligands to sequester the pollutant. This evaluation is frequently a challenging task, owing to the difficulties regarding, for example, the different number and/or nature of complexes formed. This last aspect is

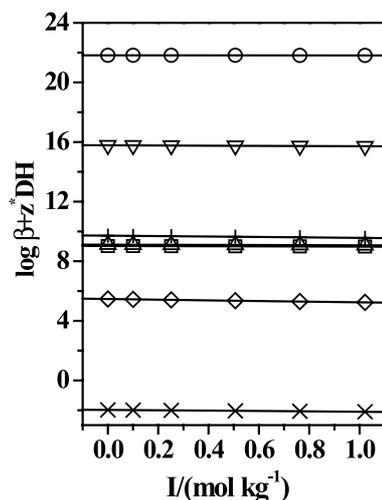


Fig. 7. Dependence on ionic strength of the stability constants of the UO_2^{2+} -Cit complexes in NaCl aqueous solution at $t = 25^\circ\text{C}$. $\square = \text{UO}_2(\text{Cit})^-$; $\circ = (\text{UO}_2)_2(\text{Cit})_2^{2-}$; $\triangle = (\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{4-}$; $\nabla = (\text{UO}_2)_2(\text{Cit})_2(\text{OH})_2^{3-}$; $\diamond = (\text{UO}_2)_2(\text{Cit})(\text{OH})_2^-$; $+ = (\text{UO}_2)_2(\text{Cit})(\text{OH})^0$; $\times = (\text{UO}_2)_3(\text{Cit})_2(\text{OH})_5^{5-}$.

strictly correlated with the network of interactions occurring in a multicomponent system and, in particular, with the different complexing abilities of different ligand classes in different conditions and with competition of the proton and/or hydroxide ion with metals and ligands involved in the sequestration process.

This problem has been overcome by calculation of pL_{50} , a semi-empirical parameter that, when the conditions (pH, ionic strength, supporting electrolyte, temperature) are fixed, can give an objective representation of this binding ability. This parameter, already tested successfully for other systems [63, 64], is obtained by use of the following Boltzmann-type equation:

$$\sum(\%) = 100 \times \left[\frac{1}{1 + \exp(pL - pL_{50})} - 1 \right] \quad (7)$$

where $\sum(\%)$ is the sum of the formation percentages of all the metal-ligand complexes vs. pL , ($pL \equiv -\log [L]_{\text{tot}}$ and $[L]_{\text{tot}}$ is the total ligand concentration). This function is assimilable to a sigmoid curve (or a dose response curve) with asymptotes of 100 for $pL \rightarrow -\infty$ and 0 for $pL \rightarrow +\infty$. In particular, pL_{50} represents the ligand concentration necessary to sequester 50% of metal ion; therefore this parameter can be used as a measure of the sequestering abilities of different ligands.

It is important to note that this property varies with experimental conditions, but it is independent of the analytical concentration of the metal ion when this is present as a trace amount in the system. Moreover in the calculation of pL_{50} , all the side-interactions occurring in the system (metal hydrolysis, ligand protonation, interactions with other components) are taken into account in the speciation model, but are excluded from estimation of pL_{50} and do not make any contribution. Since the pL_{50} was calculated at trace concentration of metal ion, in this condition, essentially the mononuclear uranyl-citrate complexes participate to the sequestration of metal and the polynuclear ones are formed

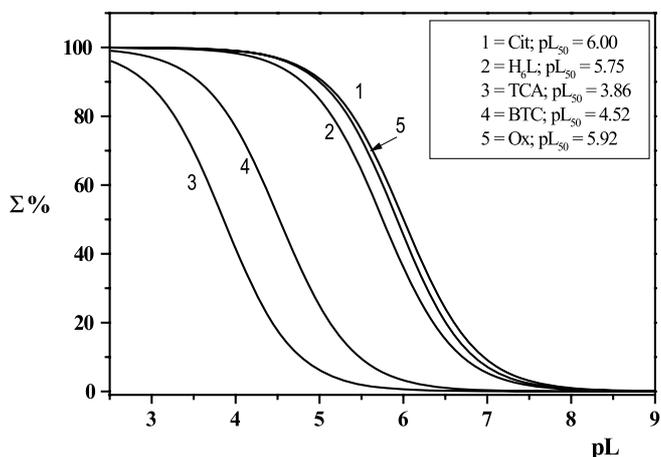


Fig. 8. Sequestration diagram for different UO_2^{2+} -polycarboxylic ligand systems. Experimental conditions: $C_{\text{UO}_2^{2+}} = 10^{-9} \text{ mol L}^{-1}$ (trace); $\text{NaCl} = 0.5 \text{ mol L}^{-1}$, $\text{pH} = 5.0$ and at $t = 25^\circ\text{C}$.

in very low amounts. The pL_{50} gives a clear picture of the sequestering ability of different ligands toward a metal.

In order to evidence and compare the sequestering ability of citrate towards UO_2^{2+} , with respect to other carboxylic ligands (namely, oxalate, 1,2,3-propanetricarboxylate, 1,2,3,4-butanetetracarboxylate and mellitate), we calculated the pL_{50} values for each uranyl-polycarboxylate system in the experimental conditions: $C_{\text{UO}_2^{2+}} = 10^{-9} \text{ mol L}^{-1}$ (trace) and pL ranging from 2 to 9 at a given pH value ($\text{pH} = 5.0$).

From the results reported in Fig. 8, it is possible to observe as the sequestering ability of citrate toward UO_2^{2+} is quite similar to that of oxalate [60] and quite similar with respect to mellitate [61], despite this last polycarboxylic ligand is formally hexa-charged. This trend can be justified considering the number of carboxylic groups dissociated at $\text{pH} = 5.0$ and taking into account the ligand structure and the charge density of each ligand (for a much accurate discussion on this topic see our previous papers) [60, 63]. These results confirm and justify the use of citrate as chelating agent in many environmental problems.

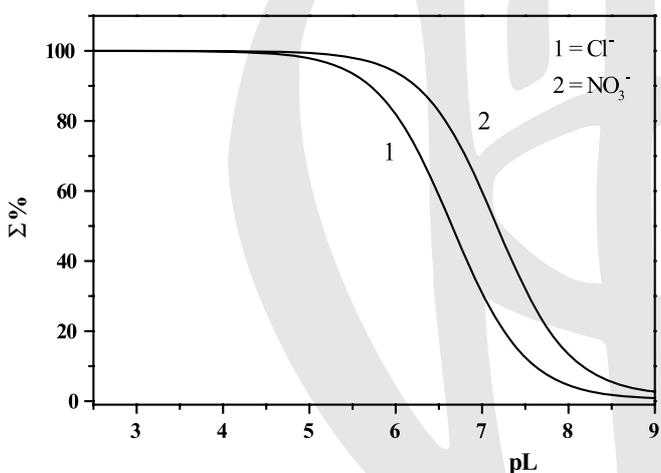


Fig. 9. Comparison between the sequestering ability of citrate toward UO_2^{2+} at $I = 0.1 \text{ mol L}^{-1}$ in NaCl and KNO_3 , respectively, and $t = 25^\circ\text{C}$. Experimental conditions: $C_{\text{UO}_2^{2+}} = 10^{-9} \text{ mol L}^{-1}$ (trace); $\text{pH} = 5.0$.

In Fig. 9, we report a comparison of the sequestering ability of citrate toward UO_2^{2+} at $I = 0.1 \text{ mol L}^{-1}$ but in two different ionic media, namely NaCl and KNO_3 , respectively. It can be observed the higher sequestering ability of citrate in KNO_3 ($pL_{50} = 7.15$) with respect to NaCl ($pL_{50} = 6.65$). The difference in the pL_{50} values can be explained taking into account the higher interacting capacity of Na^+ with respect to K^+ toward citrate; this supposition is also confirmed observing the stability constants of the UO_2 -citrate species in the two different ionic media.

The influence of Na^+ on the stability of the UO_2 -citrate species, is confirmed comparing the pL_{50} values in NaCl 0.1 mol L^{-1} ($pL_{50} = 6.00$) and 1.0 mol L^{-1} ($pL_{50} = 6.65$), respectively.

3.7 Literature comparison

Speciation of the uranyl-citrate system has been extensively studied by using different instrumental techniques such as potentiometry, UV/Vis spectrophotometry, Raman spectroscopy, NMR, EXAFS, *etc.* Recently, the scientific community has shown wide interest on radioactive element speciation and, in particular, the NEA (Nuclear Energy Agency) has collected and critically reviewed available thermodynamic data on uranium, neptunium, plutonium, americium, technetium and other fission products. The latest update on U, Np, Pu, Am and Tc was compiled in 2003 in Vol. 5 [68]. Additional efforts have been documented in 2005 in Vol. 9, where interaction of metal ions with selected organic ligands, such as oxalate, citrate, edta and isa (isosaccharinic acid) have been reviewed [28]. Despite the many publications on the interaction of actinides with organic ligands, only very few were recommended by scientific board.

The literature information about the structural data of the complexes formed by the interaction of uranyl with citrate are quite coherent among them, in particular those regarding the tendency of uranyl to form chelate complexes with citrate, and to polymerize already at relatively low concentration. In fact, Feldman *et al.* [11, 14] suggested that when equimolar mixtures of UO_2^{2+} and citrate are raised to $\text{pH} 3.5$, practically all uranyl reacts with the organic groups by tridentate chelation to form polynuclear complexes having a 1 : 1 molar ratio and held together by oxygen bridges or by hydroxyl bridges between uranium atoms. On the basis of polarographic investigation, the polymers are believed to be dimers. At slightly alkaline pH , these dimers react completely to form trinuclear complexes. Feldman *et al.* [11, 14] confirmed by ESI-MS investigations, varying UO_2^{2+} /citrate ratios, pH and counterion that for the possible trimers (namely 3 : 3 and 3 : 2, uranyl:citrate molar ratios), the stability of the 3 : 3 trimer relative to the 3 : 2 trimer decreases, probably due to an electrostatic effect. The formation of these species is favored, since the 2 : 2 species contains two ionizable COOH groups, which explain its ability to further complex uranyl and interconvert to the 3 : 2 and 3 : 3 at $\text{pH} > 4.5$.

Nevertheless, in the paper of Rajan and Martell [9], authors analyzing the potentiometric titration curves, discussed about the tendency of uranyl to polymerize with

citrate and to form some trimeric hydroxylic uranyl-citrate species at higher pH value.

The formation of the dimer and trimer species was confirmed also by Nunes *et al.* [15] and Kakihana *et al.* [36] by IR and NMR study [15]; these authors proposed also some structures for the 1:1, 2:2 species and studied the effect of pH variation on the structures of the complexes. Moreover, they proposed also the formation of the 3:2, favored with respect to other trimer species, since it assumes a cyclic trimer form. No formation constant for trimeric species has been reported up today in the literature. In every way, independently of the experimental conditions, the fundamental species in the speciation studies of the uranyl-citrate system is the $(\text{UO}_2)_2(\text{Cit})_2^{2-}$, that forms in a wide pH region from 2.5 to 9, as reported by Pasilis *et al.* [30] by Raman and mass spectroscopy studies. In these studies Pasilis *et al.* obtained only the $(\text{UO}_2)_2(\text{Cit})_2^{2-}$ species to damage of the UO_2Cit^- or $(\text{UO}_2)_2(\text{Cit})^+$, justifying this evidence with the high metal-ligand concentrations used in the studies and with the probability that these species exist at concentration below the limit of detection of Raman spectroscopy.

From these studies, Pasilis *et al.* evidenced that already at $\text{pH} \sim 2$, citrate behaves as a stronger ligand and effectively competes with OH^- for the uranyl ion, preventing the formation of insoluble species, and they observed that when pH increases, some Raman bands (at 795 and 812 cm^{-1}) increase slightly in intensity, indicating that more highly oligomerized UO_2 -citrate complexes are formed. Also at $\text{pH} > 3.5$, the bands for the uranyl hydrolytic species disappear completely and the $(\text{UO}_2)_2(\text{Cit})_2^{2-}$ species becomes the predominant one. For further increase of pH, the absence of spectral bands in the zones were the uranyl hydrolytic species form, indicates that citrate binds uranyl more strongly than OH^- , preventing the formation of significant concentration

of $(\text{UO}_2)_3(\text{OH})_5^+$ and $(\text{UO}_2)_3(\text{OH})_7^-$ species, that would be expected at $\text{pH} > 5$. The literature data above discussed are in quite good agreement with the speciation model proposed in the present study.

Logically, other uranyl-citrate complexes were proposed in other papers; for example Vaňura *et al.* [23] proposed besides the UO_2Cit^- and $(\text{UO}_2)_2(\text{Cit})_2^{2-}$, also the $(\text{UO}_2)_2(\text{Cit})_2\text{H}^-$ also the $(\text{UO}_2)_2(\text{Cit})_2\text{H}_2^0$, but at high H^+ concentration. Ohyoshi *et al.* [20] proposed other mononuclear protonated species, such as UO_2CitH^0 , $\text{UO}_2\text{CitH}_2^+$ and $\text{UO}_2\text{CitH}_3^{2+}$ in NaClO_4 0.1 mol L^{-1} , but in order to obtain these protonated species, authors prepared different solutions so as to keep the concentration of the H_3Cit^0 constant and to vary H_2Cit^- and HCit^{2-} in the pH range 2.2–2.9; nevertheless authors proposed for these species, approximate stability constants. A quite accurate discussion about the structure of the uranyl-citrate complexes was also reported by Bailey *et al.* [31].

Despite literature reports a lot of studies on the uranyl-citrate system (see Table 12), the data regarding the stability constants of the species formed from the interaction between these two components appear often discordant both in term of speciation model that of $\log \beta_{pqr}$ values.

The large part of the thermodynamic data, published some decades ago (see Table 12), were determined in different ionic media, temperatures, experimental conditions. Only Bronikowski *et al.* [22] reported the $\log \beta_{pqr}$ values for the uranyl-citrate system at different ionic strengths values in NaCl aqueous solution, but in this paper authors reported only the $\log \beta_{pqr}$ values for the UO_2Cit^- . No indication are reported about other possible species such as $(\text{UO}_2)_2(\text{Cit})_2^{2-}$.

Rajan and Martell [9] studied 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} . They reported that the polynuclear complexes are formed in which bridging between metal ions

Table 12. Literature data for stability constants of the uranyl-citrate system.

	$\log \beta$	$t/^\circ\text{C}$	I^a/medium	Ref.
$\text{UO}_2^{2+} + \text{Cit}^{3-} = \text{UO}_2(\text{Cit})^-$	3.16	25	–	[12]
	8.50	25	0.15 M NaCl	[19]
	7.40	25	0.1 M KNO_3	[9]
	6.87	25	1.0 M KNO_3	[9]
	5.78	25	1.0 M KNO_3	[19]
	7.22	25	0.1 M $\text{Na}(\text{H}_2\text{Cit})$	[20]
	6.20	25	1 M (H, Na, $(\text{UO}_2)_{0.5}$) $_3\text{Cit}$	[23]
	7.17	25	Not specified	[23]
	3.93	20	0.05 M NaClO_4	[21]
	7.30	25	0.3 m NaCl	[22]
	7.08	25	1.0 m NaCl	[22]
	7.22	25	2.0 m NaCl	[22]
	7.10	25	3.0 m NaCl	[22]
	7.02	25	4.0 m NaCl	[22]
	7.03	25	5.0 m NaCl	[22]
6.69	21	0.1 M NaClO_4	[17]	
$2\text{UO}_2^{2+} + 2\text{Cit}^{3-} = (\text{UO}_2)_2(\text{Cit})_2^{2-}$	19.26	25	0.136 M KNO_3	[14]
	18.87	25	0.1 M KNO_3	[9]
	17.70	25	1.0 M KNO_3	[9]
	18.90	25	0.15 M NaCl	[19]
	17.57	25	1.0 M KNO_3	[19]
	15.25	25	1 M (H, Na, $(\text{UO}_2)_{0.5}$) $_3\text{Cit}$	[23]

a: mol L^{-1} .

occurs through carboxylates and hydroxylic groups of the ligand. Moreover they observed that the values of $\log \beta_{pq}$ increase with increasing of the metal concentration; such trend indicates that polymerization reaction may be taking place in solution. Ohyoshi *et al.* [20], studying the speciation of the uranyl-citrate system by cation exchange resin, observed that the stability constant value is a decreasing function of the pH. This again confirms that the experimental conditions influence strongly the stability and speciation of the species. Among all the literature data published on the stability of the uranyl-citrate species in different conditions such as ionic strength and ionic media, the only paper worthy of mentions are those of Bronikowski *et al.* [22] and Rajan and Martell [9]. The investigations were carried out in different ionic media, such as NaCl and KNO₃, respectively, and at the same ionic strength authors report quite different values for the stability constant of the UO₂Cit⁻ species. For example Rajan and Martell [9] reported at $I = 1.0 \text{ mol L}^{-1}$, for the UO₂Cit⁻ species, $\log \beta_{110} = 6.87$ against a values of 7.40 at $I = 0.1 \text{ mol L}^{-1}$. For the (UO₂)₂(Cit)₂²⁻, we have, $\log \beta_{220} = 18.87$ and 17.70 at $I = 0.1$ and 1.0 mol L^{-1} , respectively. Bronikowski *et al.* [22] at $I = 1.0 \text{ mol L}^{-1}$ in NaCl reported: $\log \beta_{110} = 7.08$. Li *et al.* [18] reported instead in NaCl at $I = 0.15 \text{ mol L}^{-1}$ and between pH 1.9–2.5 where the species H₂Cit⁻ is the dominant species, a value of $\log \beta_{110} = 8.5$. Lenhart *et al.* [17] reported at 0.1 mol L^{-1} in NaClO₄ for the UO₂Cit⁻ a values of 6.69. Other studies were carried out by Vaňura *et al.* [23] in 1.0 mol L^{-1} Na₃Cit at different pH values; they suggested for these species a value of 7.17, and also proposed the stability constants for the UO₂CitH⁰ and (UO₂)₂(Cit)₂²⁻ species that are: 9.81 and 17.00, respectively. On the basis of the literature data reported, it is difficult to make a comparison both in term of speciation model and of stability constants or dependence on ionic strength. The only comparison that can be done regards the UO₂Cit⁻ and (UO₂)₂(Cit)₂²⁻ species at $I = 0.1$ and 1.0 mol L^{-1} . Taking into account the discussion above reported as regards the dependence of the stability constants on the experimental conditions used (pH, component concentration, ligand/metal molar ratio, ionic strength, ionic media), the data here reported can be considered in good agreement with those reported by Rajan *et al.* [9], Ohyoshi *et al.* [20] and Bronikowski *et al.* [22] for the UO₂Cit⁻ species. Similarly, for the (UO₂)₂(Cit)₂²⁻ species, our data are comparable with the stability constants reported by Feldman *et al.* [14], Rajan *et al.* [9] and Li *et al.* [18] at $I \sim 0.1 \text{ mol L}^{-1}$ in different ionic media, as well as the corresponding value at $I = 1.0 \text{ mol L}^{-1}$; in this case our value is very close to the values reported by Markovits *et al.* [19] ($\log \beta_{220} = 17.57$ in KNO₃) and Rajan *et al.* [9] ($\log \beta_{220} = 17.70$ in KNO₃).

4. Conclusions

The speciation in the uranyl-citrate system has been widely discussed with reference to the numerous literature reports. The speciation model proposed is supported not only by results obtained with the classical potentiometric technique, but also with other independent experimental measurements. With the aim of giving a more powerful mean for specia-

tion studies of natural fluids, the uranyl-citrate system has been investigated at different ionic strengths. For the first time a value has been determined for trimeric species, although some authors [9, 11, 13, 30] reported evidences for trimeric species. To better characterize the system, the individual spectra of the seven uranyl-citrate species were calculated starting from the experimental spectra. By means of pL₅₀ parameter, the sequestering ability of citrate towards uranyl ion has been discussed with reference to other carboxylic ligands.

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