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(Article begins on next page)



# UNIVERSITÀ DEGLI STUDI DI TORINO

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## Sequestering ability of dicarboxylic ligands towards dioxouranium(VI) in NaCl and KNO<sub>3</sub> aqueous solutions at T = 298.15 K

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**Abstract** The formation constants of dioxouranium(VI)-2,2'-oxydiacetic acid (diglycolic acid, ODA) and 3,6,9-trioxaundecanedioic acid (diethylenetrioxoxydiacetic acid, TODA) complexes were determined in NaCl ( $0.1 \leq I \leq 1.0 \text{ mol}\cdot\text{L}^{-1}$ ) and KNO<sub>3</sub> ( $I = 0.1 \text{ mol L}^{-1}$ ) aqueous solutions at T = 298.15 K by ISE-[H<sup>+</sup>] glass electrode potentiometry and visible spectrophotometry. Quite different speciation models were obtained for the systems investigated, namely:  $\text{ML}^0$ ,  $\text{MLOH}^-$ ,  $\text{ML}_2^{2-}$ ,  $\text{M}_2\text{L}_2(\text{OH})^-$ ,  $\text{M}_2\text{L}_2(\text{OH})_2^{2-}$ , for the dioxouranium(VI)-ODA system, and  $\text{ML}^0$ ,  $\text{MLH}^+$ ,  $\text{MLOH}^-$  dioxouranium(VI)-TODA system (M =  $\text{UO}_2^{2+}$  and L = ODA or TODA), respectively. The dependence on ionic strength of protonation constants of ODA and TODA and of both metal-ligand complexes was investigated using the SIT (Specific ion Interaction Theory) approach. Formation constants at infinite dilution are [for the generic equilibrium  $p \text{UO}_2^{2+} + q (\text{L}^{2-}) + r \text{H}^+ = (\text{UO}_2^{2+})_p(\text{L})_q\text{H}_r^{(2p-2q+r)}$ ;  $\beta_{pqr}$ ]:  $\log \beta_{110} = 6.146$ ,  $\log \beta_{11-1} = 0.196$ ,  $\log \beta_{120} = 8.360$ ,  $\log \beta_{22-1} = 8.966$ ,  $\log \beta_{22-2} = 3.529$ , for dioxouranium(VI)-ODA system and  $\log \beta_{110} = 3.636$ ,  $\log \beta_{111} = 6.650$ ,  $\log \beta_{11-1} = -1.242$  for dioxouranium(VI)-TODA system. The influence of etheric oxygen(s) on the interaction towards the metal ion was discussed, and this effect was quantified by means of a sigmoid Boltzman type equation that allows to define a quantitative parameter ( $pL_{50}$ ) that expresses the sequestering capacity of ODA and TODA towards  $\text{UO}_2^{2+}$ ; a comparison with other dicarboxylates was made. A visible absorption spectrum for each complex reaching a significant percentage of formation in solution (KNO<sub>3</sub> medium) has been calculated to better characterise the compounds found by pH-metric refinement.

**Keywords** Dioxouranium(VI); diglycolic acid; diethylenetrioxydiacetic acid; speciation; sequestration; complex formation constants

## 1. Introduction

The interest in the uranium chemistry is grown in the last years because of its employment as nuclear fuel. In particular, the efforts of researchers are focused to study the uranyl ion behaviour, the most stable chemical form of the element in environmental conditions. Our activity in this topic concerns the study of uranyl coordination chemistry in aqueous solution and, in particular, is aimed to formulate speciation models by the application of potentiometric and spectrophotometric techniques on uranyl containing systems in presence of an organic ligand, with a particular attention to oxygen donor groups containing ligands (for which uranyl cation shows a great affinity). In order to make our data more suitable for speciation studies of natural fluids, the investigation has been extended to different values of ionic strength. Some authors [1-3] have emphasized the importance of ether linkages in coordination chemistry of metal cations which are preferentially bound by ligands containing oxygen donor groups. Thermodynamic studies of uranyl cation complexes with 2,2'-oxydiacetic acid [4,5] suggest that the stability is enhanced by the participation of etheric oxygen in coordination.

In previous works [6-11] we took into account the interaction of uranyl ion with different classes of carboxylic ligands as acetic, oxalic, malonic, succinic, azelaic, 1,2,3-propanetricarboxylic, 1,2,3,4-butanetetracarboxylic and 1,2,3,4,5,6-benzenehexacarboxylic acids. Now two ligands have been considered, namely 2,2'-oxydiacetic acid (diglycolic acid, ODA) and 3,6,9-trioxaundecanedioic acid (diethylenetrioxydiacetic acid, TODA), that in addition to carboxylate donor groups, contain etheric oxygen(s), which can interact as well with uranyl. Both potentiometry at different ionic strengths and visible spectrophotometry have been employed, in order to better characterize the species in solution.

## 2. Experimental

### 2.1 Chemicals

2,2'-oxydiacetic acid (ODA) and 3,6,9-trioxaundecanedioic acid (TODA) were Fluka products. The stock solution of ODA has been prepared by weighing; TODA was available (Fluka, techn. product) as 90% aqueous solution and was used after purification [12]. The purity of all the standard

solutions checked by alkalimetric titrations was > 99%. The titrant/titrant solutions were prepared by diluting the stock solutions, and their concentrations were determined following the procedures reported in the section 2.4.

Uranyl nitrate hexahydrate was prepared from corresponding Fluka product (puriss. > 99.5%). The stock solution has been standardised by means of gravimetric procedure after ignition to  $U_3O_8$ .

Standard NaOH, KOH and HCl solutions were prepared by diluting Fluka concentrate products and standardized against potassium hydrogenphthalate (Fluka puriss.) and sodium carbonate (Fluka puriss.), respectively. NaCl and  $KNO_3$  (Fluka, puriss.) were used after drying in stove at  $140^\circ C$ . All solutions were prepared using grade A glassware and ultrapure water (conductivity <  $0.1 \mu S$ ).

## 2.2 Electromotive force measurements

APPARATUS A. The potentiometric measurements were performed by a Metrohm mod. 713 potentiometer equipped with combined glass electrode Metrohm. The instrumental resolution was  $\pm 0.1$  mV. The titrant (KOH or HCl) was dispensed by a automatic burette Metrohm Dosimat mod. 765 (minimum reading of  $\pm 0.001$  cm<sup>3</sup>). The experiments were carried out at  $T = 298.15 \pm 0.1$  K, ionic strength  $I = 0.1$  M ( $KNO_3$ ) and a stream of purified nitrogen was gently bubbled in the titration cell in order to avoid the interference caused by the atmospheric  $O_2$  and  $CO_2$ . Temperature control was achieved by means of a liquid circulation, in the outer chamber of the titration cell, of water from a thermocryostat (model D1-G Haake). Each titration was at least twice repeated. Concentrations of the reagents were:  $3 \leq C(UO_2^{2+})/mmol L^{-1} \leq 10$  and  $3 \leq C(L^{2-})/mmol L^{-1} \leq 20$ , with metal/ligand molar ratios  $C(UO_2^{2+})/C(L^{2-})$  ranging from 1 to 2. The electrode couple was calibrated in  $-\log[H^+]$  units (pH) employing alkalimetric titrations of hydrochloric acid with standard, carbonate free, potassium hydroxide. Ionic strength and ionic medium of the calibrating solutions were the same as the solutions being examined.

APPARATUS B. The instrumental apparatus used for the potentiometric measurements consists of a Metrohm mod. E654 potentiometer equipped with a glass electrode Orion (Ross mod. 8101) and a standard calomel electrode. The instrumental resolution was  $\pm 0.1$  mV. The whole system was controlled by a suitable computer program, which reads and saves the e.m.f. values when the

equilibrium is reached. Pre-established volumes of titrant were delivered in the measurement cell by an automatic burette Metrohm Dosimat mod. 665 (minimum reading of  $\pm 0.001 \text{ cm}^3$ ). The experiments were carried out in NaCl aqueous solutions at different ionic strength values ( $0 \leq I/\text{mol L}^{-1} \leq 1.0$ ) and  $T = 298.15 \pm 0.1 \text{ K}$ . In all the experiments, as well as with apparatus A, a stream of purified nitrogen was bubbled in the solution in order to avoid the interference caused by the atmospheric  $\text{O}_2$  and  $\text{CO}_2$ .

Measurements carried out in NaCl aqueous solutions were performed by using three different procedures; in the first, solutions containing different concentrations of uranyl ion, carboxylates and NaCl (in order to obtain the pre-established ionic strength values) were titrated with standard carbonate-free NaOH solutions until precipitation occurs; in the second, the measurement solutions containing only uranyl ion and NaCl at different concentrations were titrated with standard solutions of ODA or TODA sodium salt. In the third, the experiments were carried out at low metal and ligand concentrations without addition of the supporting electrolyte. Each titration was at least twice repeated. The potentiometric measurements were carried out at different ligand/metal molar ratios from 1.2 to 4 and in concentration ranges of:  $0.8 \leq C(\text{UO}_2^{2+})/\text{mmol L}^{-1} \leq 2.5$  and  $1.2 \leq C(\text{L}^{2-})/\text{mmol L}^{-1} \leq 15$ , where  $\text{L}^{2-}$  is ODA or TODA. For all the potentiometric measurements the electrode couple was standardized, in terms of  $\text{pH} = -\log[\text{H}^+]$ , by titrating HCl  $10 \text{ mmol L}^{-1}$  solution (having the same ionic strength value as the solution under study) with standard NaOH, to determine the standard potential  $E^\circ$ , before each experiment.

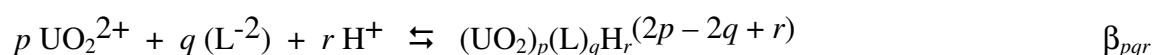
### 2.3 Spectrophotometric measurements

The visible spectrophotometric determinations were carried out with a Jasco V-550 UV/VIS spectrophotometer from 350 to 550 nm (optical path length 1.000). The solution being examined was 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, avoiding any equilibrium inconvenience. The metal concentration and the metal-to-ligand ratio were the same with regard to potentiometric determinations (APPARATUS A,  $\text{KNO}_3$  0.1 M). For each experimental condition, measurements were at least twice repeated.

### 2.4 Data analysis and calculations

To determine all parameters of the acid-base titration, the calculations were performed by using the non linear least squares computer program ESAB2M [13]. This program allow us to refine the analytical concentration of reagents, the electrode formal potential  $E^\circ$ , the coefficient  $j_a$  relative to the junction potential (according to the equation:  $E_j = j_a [H^+]$ ) and the ionic product of water  $K_w$ ; it was also used for the determination of carboxylates purity. The formation constant values were refined by the computer program BSTAC [14] which minimizes the error squares sum on electromotive force values. This program is able to perform calculations in not constant ionic strength conditions by using a simple approach already described [14]. If all the interactions between the metal and the ligand under study with the ions of the supporting electrolyte are taken into account, we may obtain quite accurate values of formation constants at infinite dilution.

All the formation constants are expressed according to the equilibrium:



Spectrophotometric data were analysed by means of the HYPERQUAD software[15], which calculates the values of molar absorption ( $\epsilon_\lambda$ ) by using experimental spectra (absorbance,  $A$ , vs. wavelength,  $\lambda/\text{nm}$ ), analytical concentrations of the reagents and the chemical model (stoichiometric coefficients and known 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,  $\epsilon/\text{mol}^{-1}\text{L cm}^{-1}$ , vs. wavelength,  $\lambda/\text{nm}$ ), only assuming the additivity of the absorbance in the investigated concentration range (Lambert-Beer's law). Experimental spectra are then re-built starting by the calculated one (using the concentration by the species distribution) and a statistical comparison give 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.

For the formation constants relative to hydrolysis reactions and the visible absorption spectra referred to uranyl ion and single hydrolytic species, our previous values [6] have been employed.

## 2.5 Dependence of stability constants on ionic strength

The stoichiometric formation constants of  $\text{UO}_2^{2+}$ -dicarboxylates species, can be expressed by (charges omitted for simplicity):

$$\log \beta_{\text{pqr}} = \log {}^T\beta_{\text{pqr}} + p \log \gamma_{\text{UO}_2} + q \log \gamma_{\text{L}} + r \log \gamma_{\text{H}} - \log \gamma_{(\text{UO}_2)_p\text{L}_q\text{H}_r} + j \log a_w \quad (1)$$

where  $\gamma_i$  is the activity coefficient of the  $i$ -th component and  ${}^T\beta_{\text{pqr}}$  is the formation constant at infinite dilution,  $\log a_w$  is the activity coefficient of water and  $j$  is the number of water molecules involved in the equilibrium. The determination of thermodynamic formation constants of  $\text{UO}_2^{2+}$ -dicarboxylate species requires a suitable equation for the dependence of activity coefficients on ionic strength. In this work, the dependence of molal formation constants on ionic strength was investigated by means of SIT (Specific ion Interaction Theory) equation [16-17], and calculations were carried out by using LIANA computer program [18].

According to the SIT approach [16-17], the activity coefficients of a cation or an anion can be expressed as:

$$\log \gamma = -z^2 \frac{AI^{1/2}}{1+1.5I^{1/2}} + \sum \varepsilon m_i \quad (2)$$

where  $A$  = Debye-Hückel constant = 0.51 at  $T=298.15$  K,  $\varepsilon$  is the interaction coefficient and the sum is extended to the interactions between the ion under examination and all the ions  $i$  of opposite charge at the molality  $m_i$ ; for a neutral species, we have:

$$\log \gamma_{\text{N}} = k_{\text{m}} I \quad (3)$$

where  $k_{\text{m}}$  is the Setschenow coefficient [19] and  $\gamma_{\text{N}}$  its activity coefficient.

For the SIT calculations, we used for  $\text{UO}_2^{2+}\text{Cl}^-$  and  $\text{H}^+\text{Cl}^-$ , respectively, the following interaction coefficients:  $\varepsilon [\text{UO}_2^{2+}, \text{Cl}^-] = 0.25$  [7],  $\varepsilon [\text{H}^+, \text{Cl}^-] = 0.12$  [20].

Conversion [21] from molar to molal concentration scale in NaCl aqueous solution was obtained using the following equations at  $T = 298.15$  K ( $c$  = molar concentration;  $m$  = molal concentration)

$$c/m = d_0 + a_1c + a_2c^2$$

$$\text{with } d_0 = 0.99987 \text{ g/cm}^3; a_1 = -0.017765; a_2 = -6.525 \cdot 10^{-4}$$

valid in the range:  $0 \leq I(\text{NaCl}) \leq 6.0 \text{ mol kg}^{-1}$ .

### 3. RESULTS AND DISCUSSION



### 3.1 Hydrolysis of dioxouranium(VI) and protonation constants

The equilibrium constants for the hydrolysis of  $\text{UO}_2^{2+}$  in NaCl aqueous solution at different ionic strength and  $T = 298.15 \text{ K}$  were already determined by potentiometric measurements [22-23]; data in  $\text{KNO}_3$  were obtained from Ref. 6.

The speciation model for the hydrolytic species of  $\text{UO}_2^{2+}$  in NaCl aqueous solution is quite different with respect to  $\text{KNO}_3$  aqueous solutions; in fact if the first supporting electrolyte was used, the speciation is characterized by the presence of several species, namely: the mononuclear hydrolytic species  $\text{UO}_2\text{OH}^+$ , generally formed at low uranyl concentrations; the binuclear hydrolytic species  $(\text{UO}_2)_2(\text{OH})_2^{2+}$ , the threenuclear hydrolytic 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 only in chloride media by the formation of a fairly stable ion pair  $(\text{UO}_2)_3(\text{OH})_4\text{Cl}^+$  [22]. In  $\text{KNO}_3$  aqueous solutions, two uranyl hydrolytic species are enough to fully explain the trend of the pH-metric titrations, namely:  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  and  $(\text{UO}_2)_3(\text{OH})_5^+$  [6].

The ligand protonation constants were determined in  $\text{KNO}_3$  ( $I = 0.1 \text{ mol L}^{-1}$ ), while those in NaCl (at different ionic strengths) were reported in previous papers [24-25]. The values are collected in Table 1 in the molar and molal concentration scales.

### 3.2 $\text{UO}_2^{2+}$ - ODA complexes

The refinement of potentiometric data, both in  $\text{KNO}_3$  and in NaCl at different ionic strengths shows the presence in solution of five species, namely  $\text{UO}_2(\text{ODA})^\circ$ ,  $\text{UO}_2(\text{ODA})_2^{2-}$ ,  $\text{UO}_2(\text{ODA})\text{OH}^-$ ,  $(\text{UO}_2)_2(\text{ODA})_2\text{OH}^-$  and  $(\text{UO}_2)_2(\text{ODA})_2(\text{OH})_2^{2-}$ . The values of formation constants are listed in Table 2. With regards to ML complex ( $M = \text{UO}_2^{2+}$ ;  $L = \text{ODA}$ ), its stability is significantly higher than that of corresponding complex of glutaric acid [26] (if excluding the coordination by etheric oxygen, the dimensions of the chelating ring should be the same for ODA and glutaric acid) and confirms the previous suggestions [1-4] about the participation of etheric oxygen in coordination. In addition to the above species, we also found  $\text{MLOH}$ ,  $\text{M}_2\text{L}_2\text{OH}$  and  $\text{M}_2\text{L}_2(\text{OH})_2$  hydrolytic complexes. In particular the dimer formation further confirms the tendency of low molecular weight bicarboxylates (we have found a dimeric species for both malonate and succinate as well [6]) and also the participation of etheric oxygen in the complex formation, as the stability constant for  $\text{M}_2\text{L}_2(\text{OH})_2$  ( $\log\beta_{22-2} = 2.43$ , at  $I = 0.1 \text{ mol L}^{-1}$ ) is sensibly higher than that determined for succinate ( $\log\beta_{22-2} = 1.40$ , at  $I = 0.1 \text{ mol L}^{-1}$ ), which should form more favourable chelate rings, in the

absence of coordination by etheric oxygen. An inspection of the literature shows a good agreement with the report of Jiang *et al* [4] which have evidenced the formation of dimeric species also by using EXAFS spectroscopy, while Rao *et al* [5], in a thermodynamic study at different temperatures have evidenced only monomeric species. Fig. 1 reports a distribution diagram for all the species involved in the speciation model of the uranyl-ODA system; as can be seen, in the pH range from 2 to ~5.5, the  $\text{UO}_2\text{-ODA}^0$  is the main species and reaches about 92% at pH < 4. The other metal-ligand species are all formed in significant amounts, especially the  $(\text{UO}_2)_2(\text{ODA})_2(\text{OH})_2^{2-}$  whose formation percentages reaches ~ 45% at pH ~ 6. However, despite ODA presents in its structure an etheric oxygen that cause an increasing in the sequestering ability with respect to other dicarboxylates, it can be considered as a weak sequestering agent towards  $\text{UO}_2^{2+}$ , and this is confirmed observing the distribution diagrams at pH > 5.5, where the simple hydrolytic species of uranyl are formed in high percentage; in particular the  $(\text{UO}_2)_3(\text{OH})_5^{2+}$  (~20%) and the  $(\text{UO}_2)_3(\text{OH})_7^+$  (~80%).

An example of experimental visible spectra at different pH values for uranyl-ODA system is reported in Fig 2. Both the little bathochromic effect with raising pH value (and the complex formation) and the scarce resolution of the absorption uranyl band after coordination are nearly the same as outlined in our previous paper [6] concerning uranyl complexes of acetate, malonate and succinate. The elaboration of all the spectrophotometric data registered for each system allowed us to calculate the values of  $\lambda_{\text{max}}$  (nm) and  $\epsilon_{\text{max}}$  ( $\text{mol}^{-1} \text{L cm}^{-1}$ ) referred to the different complexes in solution. They are collected in Table 3 and confirm the slight bathochromic shift with the substitution of water molecules by more strong coordinating groups. In addition, an inspection of Fig 2 and 3 shows that the weak bands of uranyl oxocation, which appear for  $\lambda > 440 \text{ nm}$ , exhibit a relative intensity (with respect to the maximum of absorbance) significantly higher for ODA. If we look over uranyl complexes of other carboxylate ligands such as acetate, malonate, succinate, citrate, malate and tartrate, this increased relative intensity may be regarded as a singularity of ODA.

### 3.3 $\text{UO}_2^{2+}$ - TODA complexes

The species formed in solution by TODA are all monomeric, namely  $\text{UO}_2\text{H(TODA)}^+$ ,  $\text{UO}_2(\text{TODA})^\circ$  and  $\text{UO}_2(\text{TODA})\text{OH}^-$ . The values of formation constants are listed in Table 4. With regard to ML complex ( $\text{M} = \text{UO}_2^{2+}$ ;  $\text{L} = \text{TODA}$ ), the value of formation constant ( $\log\beta_{110} = 3.636$  at  $I = 0 \text{ mol L}^{-1}$ ) is significantly lower than the nearly asymptotic one ( $\log\beta_{110} = 4.1$  at  $I = 0 \text{ mol L}^{-1}$ ) estimated for

complexes formed by uranyl with bicarboxylates (oxalate, malonate, succinate, glutarate, adipate, pimelate, suberate and azelate), but is also significantly higher than the value determined for acetate ( $\log\beta_{110} = 2.86$  at  $I = 0 \text{ mol L}^{-1}$ ). The hypothesis we put forward is that the chain length is such critical passing from azelaic acid to TODA (the chain for TODA is more long by two atomic units) that the contribution by the latter carboxylate is vanished while the higher value of constant with respect to acetate complex can be explained by the participation of etheric oxygen (that more close to carboxylate) in coordination. Very probably the steric hindrance accounts for the absence of dimeric complexes or species with two ligand molecules.

The spectra in Fig 3 are referred to the uranyl-TODA system. In addition to the above considerations, we can observe that with rising pH, the increase in absorbance values is more relevant, with respect to uranyl-ODA system. All the spectrophotometric data registered for each system have been elaborated to calculate the values of  $\lambda_{\text{max}}$  (nm) and  $\epsilon_{\text{max}}$  ( $\text{mol}^{-1} \text{ L cm}^{-1}$ ) referred to the different complexes in solution. They are collected in Table 3 and confirm the slight bathochromic shift above outlined for ODA complexes.

An inspection of the whole of the spectroscopic data further confirms the previous suggestions [6] about a small bathochromic effect after complexation of uranyl cation. Furthermore there are some hydrolytic species for which the value of  $\lambda_{\text{max}}$  is more shifted ( $(\text{UO}_2)_3(\text{OH})_5^+$ ,  $(\text{UO}_2)(\text{TODA})(\text{OH})^-$ ) and the increase in the value of  $\epsilon_{\text{max}}$  is quite significant ( $(\text{UO}_2)_3(\text{OH})_5^+$ ,  $(\text{UO}_2)(\text{ODA})(\text{OH})^-$ ,  $(\text{UO}_2)(\text{TODA})(\text{OH})^-$ ).

Similarly to the  $\text{UO}_2$ -ODA system, also in this case the simple hydrolytic species of uranyl are formed in high formation percentages. As can be seen from Fig. 4, at pH  $\sim 4.5$  the  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  reaches about 20 %, and at pH values (pH  $\sim 6$ ) of natural waters the  $(\text{UO}_2)_3(\text{OH})_5^+$  species becomes the most important one, reaching about 80% of formation. The three uranyl-TODA species have maximum formation percentages at different pH values. In particular, the  $\text{UO}_2\text{-TODA}^0$  species reaches about 25% at pH  $\approx 4$  and the  $\text{UO}_2\text{-TODA}(\text{OH})^-$  about 18% at pH  $\approx 4.8$ . Over pH  $\approx 4.5$ , it can be observed the coexistence of the metal-ligand species and of the simple hydrolytic species of uranyl, whose formation percentage are very similar; this confirm the weak sequestering ability of TODA towards  $\text{UO}_2^{2+}$ .

### 3.4 Dependence on ionic strength of equilibrium constants

To analyse the dependence of formation constants on ionic strength in NaCl aqueous solutions, we used the SIT approach [16-17]. The  $\text{UO}_2^{2+}$ -ODA and TODA molar stability constants were

converted in the molal concentration scale (see Tables 2,4) using the procedure above reported [21]. In this paper, the classic SIT model (equation 2) was used instead of the two parameters SIT model proposed in previous papers [20-21], owing to the short ionic strength interval here investigated. Calculations performed using the two parameters model showed no improvement.

The variations in stability constant values with changing ionic strength can be interpreted in terms of activity coefficient variation. Using the SIT approach, the parameters for the dependence on ionic strength of  $\text{UO}_2^{2+}$ -ODA and -TODA species were calculated and the corresponding values are reported in Table 5 (SIT parameters, for hydrolytic constants of uranyl were already reported [7]) whilst the SIT parameters for ODA and TODA protonation constants were calculated in this paper (Table 5); in this case interaction parameter ( $k_m$ ) for the neutral species ( $\text{H}_2\text{L}^0$ ) of dicarboxylates was assumed equal to zero and then neglected in the calculation.

### 3.5 Sequestering ability of dicarboxylates towards dioxouranium(VI)

In some previous papers [9-11], we proposed a Boltzman type equation which allows to calculate a quantitative parameter that defines the sequestering ability of a ligand towards a metal by means of a function of the sum of formation percentages of all metal-ligand complexes,  $\Sigma(\%)$ , vs.  $pL$ , where  $pL \equiv -\log [L]_{\text{tot}}$  ( $[L]_{\text{tot}}$  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  $pL \rightarrow +\infty$ :

$$\Sigma(\%) = 100 \times \left[ \frac{1}{1 + \exp[(pL - pL_{50})/S]} - 1 \right] \quad (4)$$

in this equation are present two empirical parameters; the former is the parameter  $S$  that is a measure of the slope in the flex of the function  $\Sigma(\%)$  vs.  $pL$ ; the latter, more important, is the  $pL_{50}$  parameter that represents the ligand concentration necessary to sequester 50 % of metal ion. This parameter is very useful because it gives a clear quantification of the amount of metal yet free (not bound to the ligand) in different experimental conditions, such as: ionic strength, ionic medium, pH and temperature; moreover it allows to compare the sequestering ability of different ligands towards one or more metals and to quantify the strength of the interaction of metal-ligand systems having quite different speciation models, independently of the type of complexes formed.

In order to evidence the different sequestering ability of dicarboxylic ligands towards  $\text{UO}_2^{2+}$ , we calculated the  $pL_{50}$  values for each uranyl-dicarboxylate (oxalate [8], malonate [6], succinate [6], azelate [6], ODA and TODA) system by means of the function  $\Sigma(\%)$  vs.  $pL$  in the experimental conditions:  $C_{\text{UO}_2^{2+}} = 10^{-9} \text{ mol L}^{-1}$  (trace) and  $pL$  ranging from 2 to 9 in NaCl aqueous solutions at three different pH values, namely: 4.0, 5.0 and 7.0. As an example, Fig. 5 reports the  $pL_{50}$  values obtained for the systems investigated at  $\text{pH} = 5.0$ , whilst Table 6 reports the  $pL_{50}$  at the three different pHs. As can be seen, at  $\text{pH} = 4.0$  and  $5.0$  ( $\text{pH}$  values experimentally investigated for all the  $\text{UO}_2$ -ligand systems), the  $pL_{50}$  values follows a systematic trend, namely its values is inversely proportional to the alkyl chain length. In particular the dicarboxylic ligand that mostly sequester  $\text{UO}_2^{2+}$ , in this experimental conditions, is oxalate, and the less interacting towards the metal ion is TODA. Taking into account all the dicarboxylates we have:

$$pL_{50}: \text{Ox} (5.9) > \text{Mal} (4.9) > \text{ODA} (4.8) > \text{Succ} (3.5) > \text{Aze} (3.1) > \text{TODA} (2.8)$$

Since for some metal-ligand systems (namely: TODA, Succ and Aze) precipitation was observed at  $\text{pH} < 7.0$ , the  $pL_{50}$  values determined (extrapolated) in these conditions, can be considered as rough estimates.

From this trend, as already described in previous papers [8-11], and suggested in this work, the stability constants values and the sequestering ability of different ligand classes towards uranyl depends on some factors, such as: (a) the charge density and the length of alkyl chain of carboxylates; (b) the number and the dimension of chelate ring(s); (c) the complex charge; (d) 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).

The contribution to the stabilization of metal-ligand species by the presence of etheric oxygen(s) in the ligand structure is confirmed, for example, if we compare the sequestering ability of succinate [ $\text{HOOC-CH}_2\text{-CH}_2\text{-COOH}$ ] and ODA [ $\text{HOOC-CH}_2\text{-O-CH}_2\text{-COOH}$ ]. A simple comparison between  $pL_{50}$  values of ODA and Succ at  $I = 0.5 \text{ mol L}^{-1}$  in NaCl and  $\text{pH} = 5.0$  allows to observe a difference of  $\sim 1.34$  log units, and this difference can be attributed to the effect of etheric oxygen of ODA presents in the intra-carboxylic chain. As regards TODA, the sequestering ability is the lowest, even lower than that of azelate. Therefore the contribution to co-ordination by the etheric group close to carboxylate is less effective than the contribution of the second carboxylate in azelate, as above pointed out. On the other hand the sequestering ability of TODA towards  $\text{UO}_2^{2+}$  if compared in the same experimental conditions ( $I = 0.5 \text{ mol L}^{-1}$  in NaCl and  $\text{pH} =$

5.0) to that of acetate ( $pL_{50} = 2.4$ ) [7] confirms the involvement of adjacent etheric group in coordination. A similar comparison can be made between  $UO_2$ -ODA and  $UO_2$ -glutaric systems, in the similar experimental conditions with respect to the others systems investigated. In this case we obtained for  $UO_2$ -glutaric system,  $pL_{50} = 3.2$ . The chelate rings that can be formed from the interaction of glutaric acid with the metal ion, involve the same number of atoms, but with the substitution of a methylenic groups for an oxygen (ODA). The  $pL_{50}$  values obtained confirm the higher influence of etheric oxygen in the interaction towards uranyl, with respect to the length of alkyl chain of dicarboxylates.

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**Table 1** Protonation constants of ODA<sup>a)</sup> and TODA<sup>b)</sup> at different ionic strengths in NaCl aqueous solutions and at I = 0.1 mol L<sup>-1</sup> in KNO<sub>3</sub>, at T = 298.15 K

I/mol L <sup>-1</sup>	logβ <sub>1</sub> <sup>H</sup>	logβ <sub>2</sub> <sup>H</sup>	I/mol kg <sup>-1</sup>	logβ <sub>1</sub> <sup>H</sup>	logβ <sub>2</sub> <sup>H</sup>
ODA					
0.100	3.94	6.72	0.100	3.94	6.72
0.250	3.83	6.59	0.252	3.82	6.58
0.500	3.76	6.52	0.506	3.75	6.51
0.750	3.72	6.49	0.763	3.71	6.47
1.000	3.70	6.47	1.022	3.69	6.45
KNO <sub>3</sub>					
0.100 <sup>c)</sup>	3.933 ±0.006	6.782±0.009			
TODA					
0.100	3.81	6.88	0.100	3.81	6.87
0.150	3.75	6.78	0.151	3.75	6.78
0.250	3.70	6.69	0.252	3.70	6.69
0.510	3.67	6.57	0.516	3.67	6.56
0.770	3.68	6.52	0.783	3.67	6.50
1.050	3.71	6.49	1.074	3.70	6.47
KNO <sub>3</sub>					
0.100 <sup>c)</sup>	3.807±0.005	6.88±0.01			

<sup>a)</sup> Ref. 24;

<sup>b)</sup> Ref. 25;

<sup>c)</sup> this work

**Table 2** Formation constants of  $\text{UO}_2^{2+}$ -ODA system in NaCl and  $\text{KNO}_3$  aqueous solutions at different ionic strengths and  $T = 298.15 \text{ K}$

$I/\text{mol L}^{-1}$	$\log \beta_{110}$ ( $\pm 0.003$ ) <sup>a)</sup>	$\log \beta_{11-1}$ ( $\pm 0.005$ ) <sup>a)</sup>	$\log \beta_{120}$ ( $\pm 0.03$ ) <sup>a)</sup>	$\log \beta_{22-2}$ ( $\pm 0.02$ ) <sup>a)</sup>	$\log \beta_{22-1}$ ( $\pm 0.02$ ) <sup>a)</sup>
0	6.146	0.196	8.36	3.53	8.97
0.10	5.289	-0.460	7.47	2.41	7.48
0.25	5.025	-0.678	7.15	2.01	7.05
0.50	4.836	-0.853	6.88	1.66	6.77
0.75	4.744	-0.956	6.70	1.43	6.65
1.00	4.694	-1.027	6.57	1.26	6.61

$I/\text{mol kg}^{-1}$	$\log \beta_{110}$	$\log \beta_{11-1}$	$\log \beta_{120}$	$\log \beta_{22-2}$	$\log \beta_{22-1}$
0.100	5.287	-0.460	7.465	2.410	7.480
0.252	5.022	-0.678	7.148	2.011	7.045
0.506	4.831	-0.853	6.869	1.658	6.756
0.763	4.737	-0.956	6.686	1.427	6.636
1.022	4.685	-1.027	6.547	1.249	6.590

$I/\text{mol L}^{-1}$	$\text{KNO}_3$				
0.10	5.235(4)	-0.46(3)	7.560(7)	2.26(2)	7.45(1)

<sup>a)</sup>  $\pm$  Std. dev.

**Table 3** Values of  $\lambda_{\max}$  (nm) and  $\epsilon_{\max}$  ( $\text{mol}^{-1} \text{L cm}^{-1}$ ) for  $(\text{UO}_2)_p\text{L}_q\text{H}_r$  complexes (L = ODA or TODA) at T = 298.15 K and I = 0.1 mol L<sup>-1</sup>

species	$\lambda_{\max}$	$\epsilon_{\max}$ <sup>a)</sup>
$(\text{UO}_2)(\text{ODA})^\circ$	420	14
$(\text{UO}_2)(\text{ODA})_2^{2-}$	423	23
$(\text{UO}_2)(\text{ODA})\text{OH}^-$	423	56
$(\text{UO}_2)_2(\text{ODA})_2\text{OH}^-$	420	24
$(\text{UO}_2)_2(\text{ODA})_2(\text{OH})_2^{2-}$	422	51
$(\text{UO}_2)(\text{TODA})\text{H}^+$	419	22
$(\text{UO}_2)(\text{TODA})^\circ$	420	20
$(\text{UO}_2)(\text{TODA})\text{OH}^-$	430	79

<sup>a)</sup> The uncertainty estimated on  $\epsilon_{\max}$  values ranges between 2 and 8% ( $\pm 3s$ ), according to the formation percentage of each single complex reached in solution.

**Table 4** Formation constants of  $\text{UO}_2^{2+}$ -TODA system in NaCl aqueous solutions at different ionic strengths and  $T = 298.15 \text{ K}$

$I/\text{mol L}^{-1}$	$\log \beta_{110}$ ( $\pm 0.003$ ) <sup>a)</sup>	$\log \beta_{111}$ ( $\pm 0.006$ ) <sup>a)</sup>	$\log \beta_{11-1}$ ( $\pm 0.007$ ) <sup>a)</sup>
0	3.636	6.650	-1.242
0.10	2.787	5.787	-1.884
0.25	2.535	5.514	-2.080
0.50	2.366	5.310	-2.220
0.75	2.294	5.203	-2.286
1.00	2.264	5.138	-2.321

$I/\text{mol kg}^{-1}$	$\log \beta_{110}$	$\log \beta_{111}$	$\log \beta_{11-1}$
0.100	2.785	5.783	-1.884
0.252	2.532	5.508	-2.080
0.506	2.361	5.300	-2.220
0.763	2.287	5.188	-2.286
1.022	2.255	5.119	-2.321

$\pm$  Std. dev.

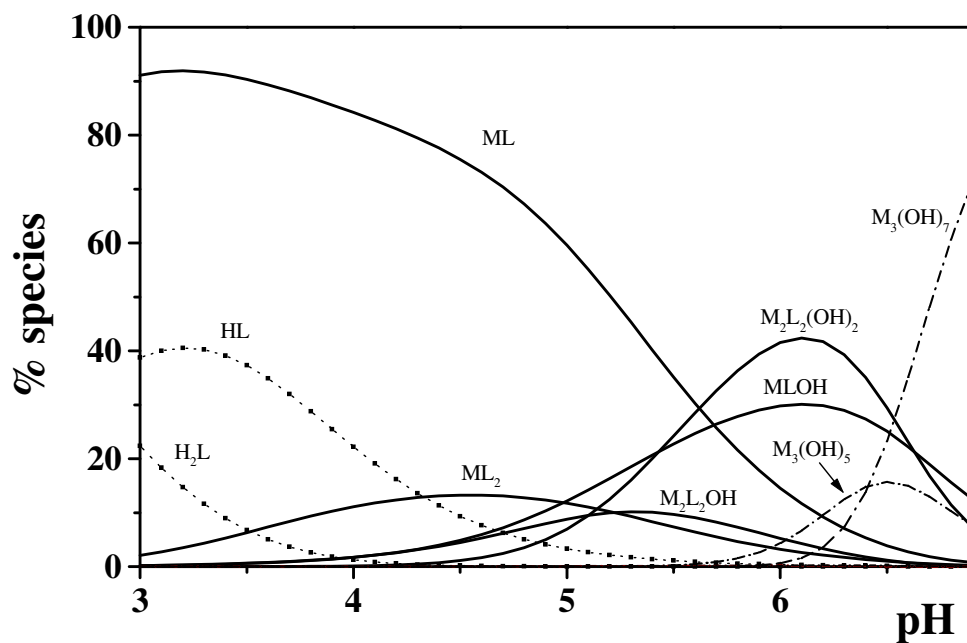
**Table 5** Specific interaction coefficients for the protonation and complexes with  $\text{UO}_2^{2+}$  of ODA and TODA systems in NaCl aqueous solutions and  $T = 298.15 \text{ K}$

SIT parameter			
species	ODA	species	TODA
$\text{L}^{2-}$	$\epsilon[\text{L}^{2-}, \text{Na}^+] = 0.151 \pm 0.016$	$\text{L}^{2-}$	$\epsilon[\text{L}^{2-}, \text{Na}^+] = -0.105 \pm 0.009$
$\text{HL}^-$	$\epsilon[\text{HL}^-, \text{Na}^+] = 0.109 \pm 0.018$	$\text{HL}^-$	$\epsilon[\text{HL}^-, \text{Na}^+] = -0.236 \pm 0.014$
UO <sub>2</sub> -ODA		UO <sub>2</sub> -TODA	
$\text{ML}^0$	$k_m = 0.227 \pm 0.001$	$\text{ML}^0$	$k_m = -0.109 \pm 0.005$
$\text{MLOH}^-$	$\epsilon[\text{MLOH}^-, \text{Na}^+] = 0.379 \pm 0.004$	$\text{MLH}^+$	$\epsilon[\text{MLH}^+, \text{Cl}^-] = 0.155 \pm 0.002$
$\text{ML}_2^{2-}$	$\epsilon[\text{ML}_2^{2-}, \text{Na}^+] = 0.724 \pm 0.006$	$\text{MLOH}^-$	$\epsilon[\text{MLOH}^-, \text{Na}^+] = -0.018 \pm 0.004$
$\text{M}_2\text{L}_2(\text{OH})_2^{2-}$	$\epsilon[\text{M}_2\text{L}_2(\text{OH})_2^{2-}, \text{Na}^+] = 0.760 \pm 0.006$		
$\text{M}_2\text{L}_2\text{OH}^-$	$\epsilon[\text{M}_2\text{L}_2\text{OH}^-, \text{Na}^+] = 0.183 \pm 0.008$		

**Table 6**  $pL_{50}$  values for the  $UO_2$ -ligand systems at  $I = 0.5 \text{ mol L}^{-1}$  in NaCl and at three different pH values

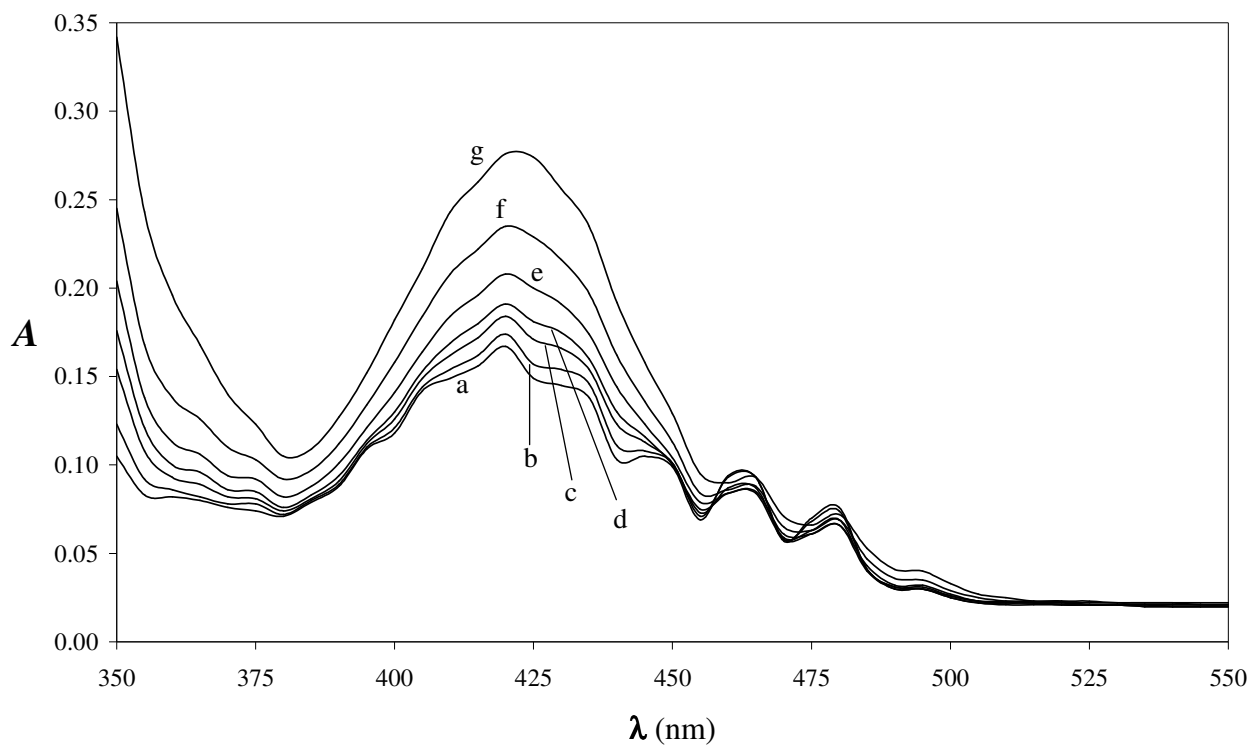
ligand	pH		
	4.0	5.0	7.0
Ox	5.8	5.9	6.4
Mal	4.2	4.9	4.1
ODA	4.7	4.8	4.9
Succ	2.6	3.5	2.7 <sup>a)</sup>
Aze	2.3	3.1	2.7 <sup>a)</sup>
TODA	2.3	2.8	3.5 <sup>a)</sup>

<sup>a)</sup> Estimated values



**Fig. 1** Distribution diagram for the system  $\text{UO}_2^{2+}$ -ODA at  $I = 0.5 \text{ mol L}^{-1}$  and  $T = 298.15 \text{ K}$  in NaCl.

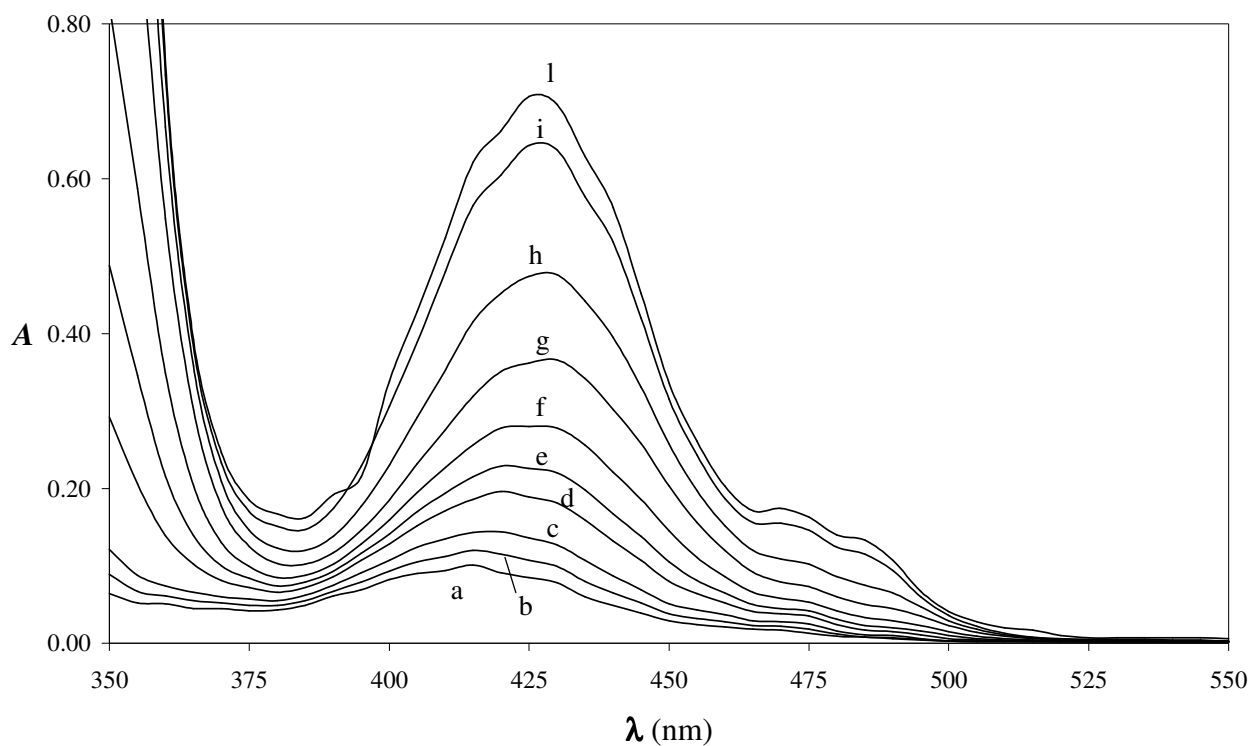
Concentration:  $C_{\text{UO}_2^{2+}} = 1.0$ ;  $C_{\text{ODA}} = 3.0 \text{ mmol L}^{-1}$ . ( $M = \text{UO}_2^{2+}$ ;  $L = \text{ODA}$ ). [charges omitted for simplicity]



**Fig. 2** Visible absorption spectra of a  $\text{UO}_2^{2+}$ -ODA system in function of pH conditions.

Concentration:  $C_{\text{UO}_2^{2+}} = 12.0 \text{ mmol L}^{-1}$ ;  $C_{\text{ODA}} = 12.0 \text{ mmol L}^{-1}$  at pH: a: 1.88; b: 2.34; c: 2.97; d: 3.59; e: 4.29; f: 4.93; g: 5.67.

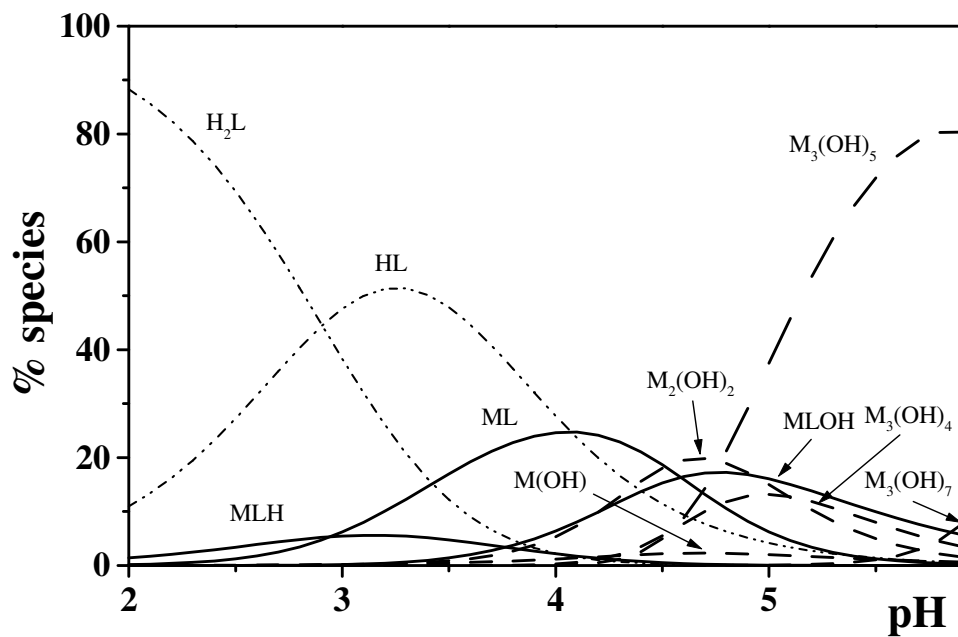




**Fig. 3** Visible absorption spectra of a  $\text{UO}_2^{2+}$ -TODA system in function of pH conditions.

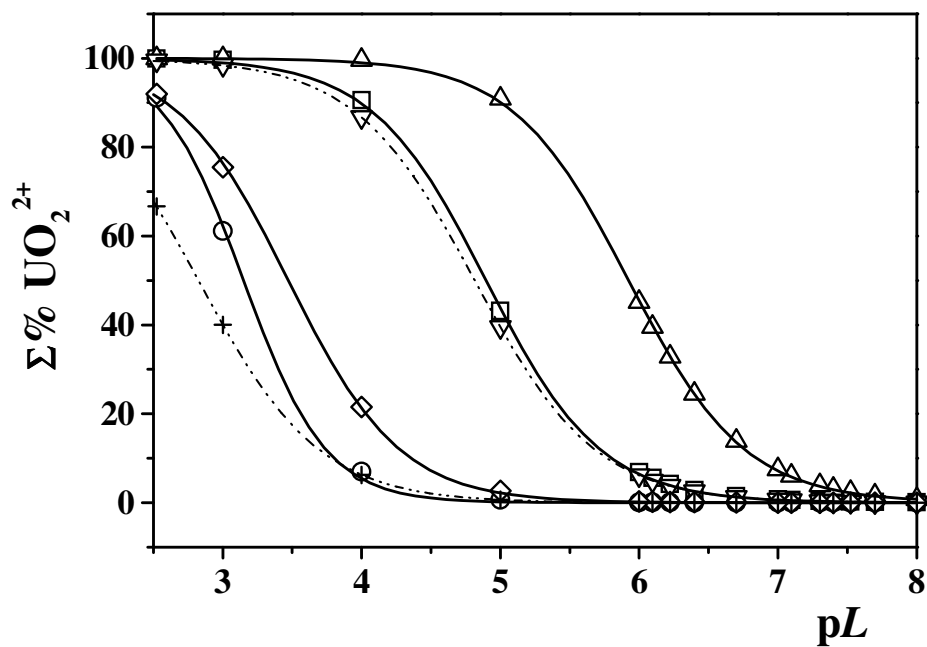
Concentration:  $C_{\text{UO}_2^{2+}} = 10.0 \text{ mmol L}^{-1}$ ;  $C_{\text{TODA}} = 10.0 \text{ mmol L}^{-1}$  at pH: a: 2.40; b: 2.92; c: 3.39; d:

3.87; e: 4.02; f: 4.17; g: 4.34; h: 4.47; i: 4.73; l: 4.92.



**Fig. 4** Distribution diagram for the system  $\text{UO}_2^{2+}$ -TODA at  $I = 0.5 \text{ mol L}^{-1}$  and  $T = 298.15 \text{ K}$  in NaCl.

Concentration:  $C_{\text{UO}_2^{2+}} = 1.0$ ;  $C_{\text{TODA}} = 3.0 \text{ mmol L}^{-1}$ . ( $M = \text{UO}_2^{2+}$ ;  $L = \text{TODA}$ ). [charges omitted for simplicity]



**Fig. 5** Sequestration diagram of  $\text{UO}_2^{2+}$ -ligand species (for the  $\text{UO}_2^{2+}$ - Ox, Mal, Succ, Aze, ODA and TODA systems) vs  $pL$ .

Experimental conditions:  $I = 0.5 \text{ mol L}^{-1}$  in NaCl and  $\text{pH} = 5.0$ .  $C_{\text{UO}_2^{2+}} = 10^{-9} \text{ mol L}^{-1}$

$pL_{50}$ :  $\Delta$  Ox = 5.9;  $\square$  Mal = 4.9;  $\nabla$  ODA = 4.8;  $\diamond$  Succ = 3.5;  $\circ$  Aze = 3.1; + TODA = 2.8