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Complex Formation of the Uranyl (UO_2^{2+}) Ion with the Diethylene Triaminopentaacetate (DTPA) Ligand at 25 °C in 3 M Sodium Perchlorate

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ABSTRACT: The complex formation between the uranyl (UO_2^{2+}) ion and the diethylene triaminopentaacetate ligand (DTPA) has been investigated at 25 °C, in a 3 M sodium perchlorate medium. The overall protonation constants β_j^H of the free ligand have been previously determined in this ionic medium: six protonated species (H_jA), with j ranging from 1 to 6, together with the free anion A^{5-} have been identified in the concentration range from $(3 \cdot 10^{-3}$ to $13 \cdot 10^{-3})$ mol·kg^{-1}. Four complex species, $H_2UO_2A^-$, HUO_2A^{2-}, UO_2A^{3-}, and UO_2AOH^{4-}, have been identified in the total uranyl concentration range from $(1.1 \cdot 10^{-3}$ to $5.7 \cdot 10^{-3})$ mol·kg^{-1}, and their overall stability constants determined, keeping the metal to ligand ratio equal to 1. Owing to the complex species formation, uranyl ions could be kept in solution until $-\log h = 7$.

INTRODUCTION

In recent years aminopolycarboxylic acids have received growing attention as multidentate ligands for inorganic cations. They are particularly useful in several practical fields because of their ability to firmly complex cations of several heavy metals, broadening the stability range of the metals in aqueous solution.

Among these ligands, diethylene triaminopentaacetic acid ($C_{14}H_{23}O_{10}N_3$) (H_5DTPA) has been largely and successfully used to chelate Gd^{3+} ions to provide a useful opaque agent in magnetic resonance imaging,[1] while its complexes with technetium (^{99m}TcDTPA) collect in the kidneys and brain, so allowing their observation by medical scintigraphy.[2] Despite the large use of DTPA in therapy and in treating soils to leach heavy metals, there is a paucity of data on its chemical behavior.

The present investigation had the aim of determining which chemical equilibria take place in aqueous solutions containing this ligand and uranyl (UO_2^{2+}) ions; which complex species are formed, the values of their stability constants, and then the dependence of the solution composition on changes in acidity.

The ionic medium 3 M has been chosen for its widespread use in equilibrium analysis;[3] accordingly, it will be easier to compare our results with those of different investigations involving the same metal ion or the same ligand. For instance, hydrolysis equilibria of the uranyl ion have been carried out in the same ionic medium.[4,5] So we could take profit of these results to correctly evaluate the extent of hydrolysis reactions in our solutions.

Moreover, the H_5DTPA ligand has been previously investigated at lower $NaClO_4$ concentrations and at different temperatures;[6−8] so, our results are of some importance to elucidate its behavior in an ionic medium in which the activity coefficients of reacting species can be considered constant.

Finally, the use of the electrochemical-potentiometric method to carry out acid−base titrations has freed us from the need to use strong base solutions, which are unavoidably exposed to carbon dioxide contamination. Titrations have been carried out adding a base to the initially acidic solution and acid to basic solutions obtained in the first part of each titration: we have always obtained reproducible results, which confirm the actual attainment of the equilibrium condition. In our opinion this has improved the accuracy of our results.

EXPERIMENTAL SECTION

Reagents. Aldrich 97 % H_5DTPA was crystallized twice from hot water. The crystals were crushed to a white powder and stored in a closed vessel.

Uranyl oxide (U_3O_8) was obtained by dissolving uranyl nitrate (Fluka puriss p.a. grade) in hot water, adding a 10 % excess of concentrated ammonia solution, under continuous stirring. A bright yellow solid was obtained, according to reaction 1:

$$2UO_2^{2+} + 2NH_3 + 3H_2O \rightleftarrows (NH_4)_2U_2O_{7(s)} + 4H^+ \qquad (1)$$

The suspension was diluted and kept warm, under stirring, for about one hour. It was then filtered without suction, washing the solid obtained with distilled water; it was then transferred to a platinum dish and dried for one hour at 100 °C and then overnight at 900 °C. A black solid was obtained, according to reaction 2, with a 97.5 % yield. It was crushed and stored in a closed vessel.

$$3(NH_4)_2U_2O_{7(s)} \rightleftarrows 2U_3O_{8(s)} + 6NH_{3(g)} + O_{2(g)} + 3H_2O_{(v)} \qquad (2)$$

Stock Solutions. All of the solutions were prepared using twice-distilled water; when not otherwise specified, analytical grade reagents and standard methods of analysis[9] were used.

Stock sodium perchlorate solutions were prepared and analyzed as described previously.[10]

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A stock uranyl perchlorate solution was obtained by mixing in a 500 mL volumetric flask weighed amounts of $NaClO_4$ stock solution, a measured volume of standard perchloric acid, and a weighed amount of solid U_3O_8. The mixture was diluted to about 400 mL with distilled water, and then ozone was bubbled to complete dissolution of the solid, which lasted a few days.

The resulting bright yellow solution was bubbled with nitrogen, to drive off the excess ozone and oxygen, and then diluted to the mark and its total weight determined. From the weighed amounts of its components and the weight of the final solution, the total concentration of each single reactant could be calculated. The initial H^+ concentration was diminished due to the amount consumed in reaction 3.

$$U_3O_8 + O_3 + 6H^+ \rightleftarrows 3UO_2^{2+} + O_2 + 3H_2O \qquad (3)$$

Dilute Solutions. Test solutions were prepared by weighing the proper amounts of the required stock solutions, diluting to the desired volume, and determining the total weight, to calculate the concentration in moles per solvent kg (molality, m), for each component in the resulting solution.

Potentiometric Measurements. Electromotive (emf) values of the cell used were measured by means of a high impedance voltmeter (Keithley, model 642); the glass electrode was a ROSS model of Orion, while the reference electrode was an Ingold calomel electrode, model 3868. It had been completely emptied of its internal solution and filled with a 0.01 M NaCl in 2.99 M $NaClO_4$ solution, to minimize the liquid junction potential. Accurate washing of the ceramic frit septum prevented any $KClO_4$ precipitation.

Electrochemical Cell. The electrochemical cell used to generate OH^- ions, consisted of a bright platinum cathode and an external anode; no significant difference was noticed in the electrolysis yield when a platinized platinum cathode was used. The anodic compartment was a modified Wilhelm bridge,[11] in which a silver electrode was dipped into a 0.05 M NaCl, 2.95 M $NaClO_4$ solution, connected to the test solution by means of a 3 M $NaClO_4$ salt bridge. The white silver deposit on platinum was separately obtained using the method of Brown.[12]

The electrolysis current was delivered from a direct current generator HP 6186C DC; its intensity was determined by measuring, by means of a Keithley 179 multimeter, the ohmic drop on a Leeds and Northrup 100 Ω resistor, put in series with the electrolytic circuitry.

An Hanart chronometer was used to determine the electrolysis time at a 0.1 s limit.

Apparatus. A weighted amount, between (30 and 40) g, of the test solution was put into a multinecked vessel; through its necks electrodes were dipped into the solution. The vessel was then introduced into an air bath kept at the temperature of (25 ± 0.1) °C, by means of a circulating water cooler and a 100 W lamp, connected through a thyristors relay to a vertex thermometer.

The test solution was left overnight, inside the bath, under nitrogen bubbling, to ensure thermostatic equilibrium and complete removal of carbon dioxide. Before entering the test solution, nitrogen was passed through three different washing bottles containing sodium hydroxide, to eliminate acid impurities, sulfuric acid, to eliminate alkaline impurities, and 3 M sodium perchlorate to saturate the gas with water vapor, in the same conditions of the test solution.

The solid H_5DTPA was added through one of the necks of the vessel by means of a glass vial which was weighed before and after the addition. The same procedure was used to introduce the uranyl solution into the vessel.

Volumetric titrations were carried out using a weight buret, which was weighed before and after each addition.

RESULTS AND DISCUSSION

Method of Investigation. All of the solutions used in the present investigation contained a high excess ($3\ \mathrm{mol \cdot dm^{-3}} \equiv 3.5\ \mathrm{mol \cdot kg^{-1}}$) of the inert electrolyte, to keep constant their ionic composition and hence the activity coefficients of the reacting species.[11]

The experiments were realized as coulometric acid−base titrations. To avoid the use of alkali solutions, the titrant OH^- ions were generated step by step according to half-reaction 4, at the platinum cathode of cell (H), connected to a direct current (dc) power supply.

$$- \mathrm{Pt|Test\ Solution} \parallel \mathrm{NaCl\ 0.5\ M, NaCl_4\ 2.5\ M|AgCl, Ag(+)} \qquad (H)$$

$$H_2O + e^- = \frac{1}{2}H_{2(g)} + OH^- \qquad (4)$$

From the electrolysis time t (in seconds), the intensity i (in Amperes) of the electrical current flowing through cell (H), and the value of the Faraday constant (96 485 Coulombs[13]), eq 5 allowed calculation of the amount of OH^- ions n_{OH^-} generated in each electrolysis step.

$$n_{OH^-} = i \cdot t / 96485 \qquad (5)$$

After each electrolysis step the emf of the cell (G) was measured:

$$\mathrm{GE|Test\ Solution} \parallel \mathrm{RE} \qquad (G)$$

$$\mathrm{GE = Glass\ electrode}$$

$$\mathrm{RE = Hg, Hg_2Cl_{2(s)}|NaCl\ 0.01\ M\ in\ NaClO_4\ 2.99\ M}$$

The present investigation was carried out by realizing, in sequence, three different steps:

(1) The titration of a solution S°, having the generic composition (where concentrations are expressed in molality, mol/solvent kg):

$$S^\circ \equiv [H^+] = H^\circ, \quad [Na^+] = (3.5 - H^\circ), \quad [ClO_4^-] = 3.5$$

to calibrate the potentiometric cell (G) by determining its standard potential ΔE° and to check the initial hydrogen ion concentration H°.

(2) The introduction into the S° solution of a weighed amount of the ligand as H_5A to get a solution S_L:

$$S_L \equiv [H^+] = H^\circ, \quad [H_5A] = A, \quad [Na^+] = (3.5 - H^\circ), \quad [ClO_4^-] = 3.5$$

where H_5A represents the H_5DTPA, to determine its protonation constants. The titration of S_L was carried out to neutralize all the protons of the ligand; then a weighed amount of a standard uranyl perchlorate solution in 3.5 m $NaClO_4$ was added to convert solution S_L to S_{ML}.

(3) The titration of S_{ML} solution,

$$S_{ML} \equiv [H^+] = H°, \quad [UO_2{}^{2+}] = B,$$
$$[A^{5-}] = A, \quad [Na^+] = (3.5 - H° - 2B),$$
$$[ClO_4{}^-] = 3.5$$

with total uranium(VI) concentration indicated as B and total ligand concentration indicated as A, to determine how the introduction of uranyl ions influenced the ligand acid base equilibria and to deduce, from the kind and the magnitude of these changes, the complex species formed and the values of the related stability constants.

S_{ML} was titrated with H^+ ions, by addition of a T° solution having the generic composition:

$$T° \equiv [H^+] = H_T, \quad [Na^+] = (3.5 - H_T),$$
$$[ClO_4{}^-] = 3.5$$

and back-titrated after reaching equilibrium, by coulometric addition of OH^- ions.

Potentiometric Measurement of the Hydrogen Ion Concentration. The hydrogen ion concentration has been determined through emf measurements of cell (G), as given by:

$$E = E' + 59.16 \log h \tag{6}$$

with

$$E' = \Delta E° + 59.16 \log \gamma_H + E_J \tag{7}$$

In eq 7 $\Delta E°$ represents the cell constant term, E_J the liquid junction potential, and γ_H the activity coefficient of the H^+ ion. As the ionic composition of the test solutions was very close to that of the solution inside the reference half-cell, the liquid junction potential E_J was always negligible. Moreover, the high and constant concentration of the ionic medium granted the constancy of the activity coefficients of all of the reacting species,[11] so that E, the emf of cell (G), could be expressed as reported in eq 6.

The constant term E', defined by eq 7, was determined, in the cell calibration step, by means of the potentiometric titration of solution S°.[14]

The E_J value depends on h, the free H^+ concentration, but as we experimentally found, it never exceeded the uncertainty limits of our emf measurements (0.1 mV), so that the term E' in eq 6 could be considered constant through each experiment. Couples of experimental data (E, t), collected during the titrations of solution S°, have been treated according to Gran method[15] to obtain the graph reported in Figure 1. As it can be seen, experimental points crowd around a straight line, whose intercept t_{eq} on the x axis allows the calculation of the starting hydrogen ion concentration $H°$ in S°, using eq 8, where $W°$ is the weight in grams of solvent water in the S° solution:

$$H° = \frac{i \cdot t_{eq}}{96485 \cdot W°} \tag{8}$$

Moreover, the slope of this straight line gives the best value of E'[14] which was in excellent agreement with the values calculated point by point. This E' value was then used in the successive steps of the experiment, to calculate h from E values, according to eq 9:

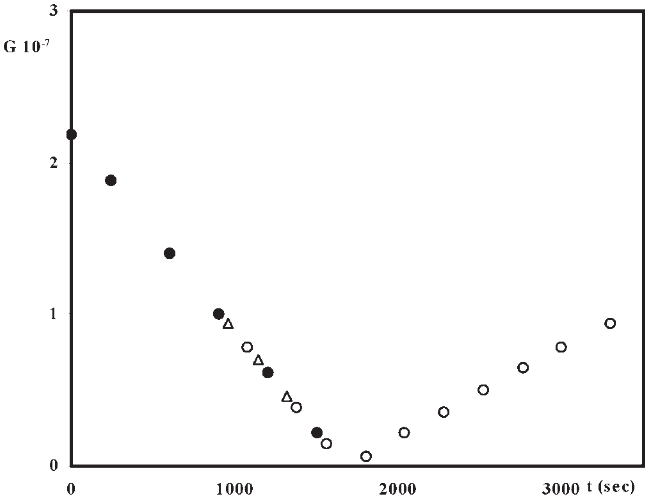

Figure 1. Gran diagram for an electrochemical titration of solution S°; ●, first alkalization; △, acidification; ○, second alkalization.

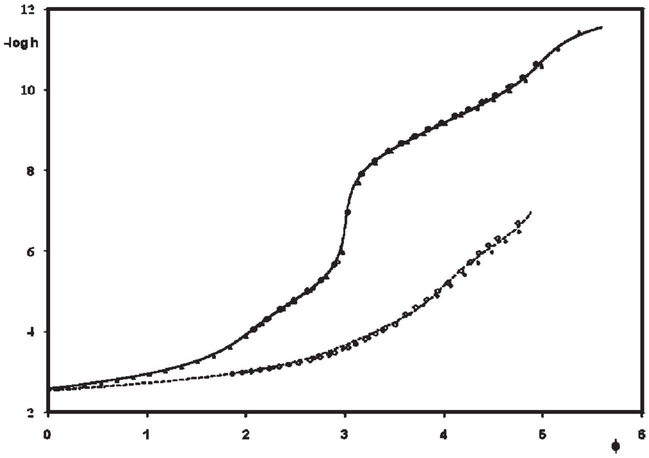

Figure 2. Comparison between the ligand and the complex titration curves. ▲, alkalization of the ligand; ●, alkalization of the ligand; ○, acidification of the ligand; —, best fit curve; ◊, acidification of the complex; ♦, alkalization of the complex; - - -, best fit curve.

$$-\log h = \frac{E' - E}{59.16} \tag{9}$$

In a few experiments, after about 70 % of the initial acidity was neutralized, the electrode polarity in cell (H) was reversed, so that H^+ ions were generated in solution, on the platinum anode according to eq 10:

$$H_2O = \frac{1}{2} O_2(g) + 2H^+ + 2e^- \tag{10}$$

Data obtained from this back-titration are reported in Figure 1 (empty triangles). As can be seen, they overlap those obtained in the first part of the titration (alkalization), represented as full circles. A further inversion of electrodes polarity led to a second alkalization, which was carried well behind the equivalent point (empty circles) to draw the ascending branch of the Gran diagram. Data in Figure 1 lie on two straight lines having the same intercept on the x axis: the slope of the descending line allows the calculation of E' and of the ionic product of water, in the used ionic medium.

From seven independent determinations, we obtained a mean value of $-\log K_w = 14.01 \pm 0.01$ at 25 °C in 3.5 m $NaClO_4$: this value has been extensively used in the present investigation to calculate $[OH^-]$ from E values.

Ligand Titration. Once the procedures to standardize cell (G) were completed, a weighed amount between (30 and 150) mg of the solid H_5DTPA ligand was added to the nearly neutralized S° solution, to obtain solution S_L. The solid completely dissolved in a few minutes, and the emf of cell (G) rapidly attained a constant value, usually higher than the one it had before the ligand addition, thereby showing an increase in the solution acidity.

The electrochemical titration of the ligand was carried out to its complete neutralization. After each OH^- addition, from the measured E value, we calculated $-\log h$ by means of eq 9, to draw the titration curves reported in Figure 2, where dots represent a complete titration and back titration.

There, $-\log h$ is reported against φ, the number of H^+ neutralized for each of the n_a moles of ligand, easily calculated, by means of eq 11, where t_{eq} is the electrolysis time needed to completely neutralize the excess of strong acid in solution S°.

$$\varphi = \frac{(t - t_{eq}) \cdot i}{96485 \cdot n_a} \qquad (11)$$

As can be seen, the titration curve of H_5DTPA shows a jump at $\varphi = 3$, corresponding to the neutralization of 3 out of 5 H^+ ions.

Once the ligand had been completely neutralized ($\varphi = 5$), increasing amounts of H^+ ions were added, to verify that our emf measurements had been carried out in conditions of true equilibrium. Unfortunately, it was not possible to realize an electrochemical in situ generation of H^+ ions, according to reaction 10, probably because the ligand is oxidized at the platinum anode. Anyway, by addition of a standard T° solution, it was possible to obtain data, reported as empty circles in Figure 2, in good agreement with those obtained during the previous electrochemical alkalization (full circles).

Titration of the Metal–Ligand Mixture. This was the last stage of our investigation and was carried out using two different (i, ii) procedures:

(i) To the solution S°, weighed amounts of the solid H_5DTPA ligand and of a stock uranyl solution having the generic composition:

$$U^\circ \equiv [UO_2{}^{2+}] = B^\circ, \quad [H^+] = H_U,$$
$$[Na^+] = (3.5 - 2B^\circ - H_U), \quad [ClO_4{}^-] = 3.5$$

were added to obtain solution S_{ML}, where the total ligand concentration A and the total metal concentration B were equal. Solution S_{ML} was then titrated by electrochemically generated OH^- ions to the complete neutralization of the five protons of the ligand and then volumetrically back-titrated, by successive additions of T°;

(ii) To solution S°, a weighed amount of the solid H_5DTPA was added; the resulting S_L solution was titrated with electrolytically generated OH^- ions to the complete neutralization of the five protons of the ligand. Then, a weighed amount of solution U° was added to obtain an S_{ML} solution with the same total ligand and metal concentrations. Solution S_{ML} was then volumetrically titrated with solution T° and electrochemically back-titrated with OH^-.

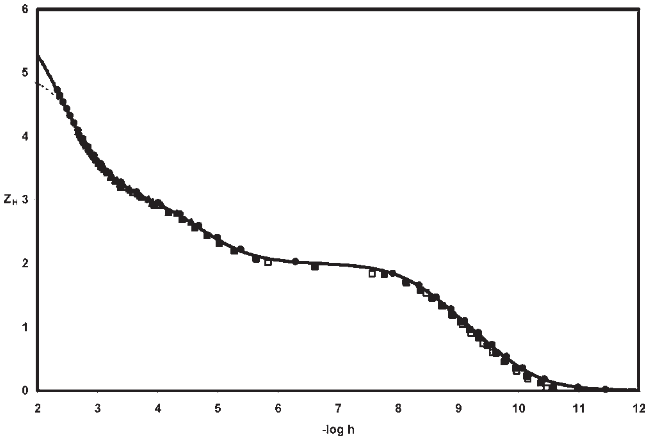

Figure 3. Protonation curve of the ligand. Empty symbols refers to volumetric titrations, full ones to electrochemical back-titrations. ▲, $A = 7.3 \cdot 10^{-3}$ m; △, $A = 7.3 \cdot 10^{-3}$ m; ■, $A = 1.9 \cdot 10^{-3}$ m; □, $A = 1.9 \cdot 10^{-3}$ m; ●, $A = 4.9 \cdot 10^{-3}$ m; —, Model I; - - -, Model II.

In Figure 2, a couple of the experimental titration and back-titration curves are compared with those of the ligand alone. Their significant differences can be ascribed to the interaction between the ligand and the uranyl ions. At corresponding φ values, the presence of uranyl ions causes an increase in the free H^+ concentration of the solution, confirming that, in the complex formation, they have taken the place of the hydrogen ions. Moreover, for $\varphi < 3$, the titration curve of the complex has the typical smoothly rising shape of a strong acid, suggesting that the complex formation reaction sets free three H^+ ions, according to eq 12:

$$UO_2{}^{2+} + H_5DTPA \rightleftarrows [H_2UO_2DTPA]^- + 3H^+ \qquad (12)$$

In the following, the uranyl ion will be denoted as M^{2+}, the ligand anion as A^{5-} and the protonated complexes as $[H_pMA]^{(p-5)}$.

In the range $3 < \varphi < 5$, the curve does not show any sharp jump, supporting the hypothesis that the weak diprotic acid $[H_2MA]^-$ loses its protons, according to:

$$[H_2MA]^- + OH^- \rightleftarrows [HMA]^{2-} + H_2O \qquad (13)$$

$$[HMA]^{2-} + OH^- \rightleftarrows [MA]^{3-} + H_2O \qquad (14)$$

The hypothesis of the formation of mixed complexes containing 2 or 1 hydrogen ions is confirmed from the shape of the protonation curve of the complexes shown in Figure 4. To better fit experimental data gathered in the less acidic range, an additional hydroxo complex species has been introduced, according to eq 15:

$$[MA]^{3-} + H_2O \rightleftarrows [MAOH]^{4-} + H^+ \qquad (15)$$

Any attempt to alkalize beyond $\varphi = 5$ caused the appearance of a pale yellow solid which slowly dissolved only by acidification of the solution to $\varphi < 5$.

■ DATA TREATMENT

Experimental data obtained from titration of solutions S_L and S_{ML} have been preliminarily treated with a traditional graphical

Table 1. Values of the Ligand Protonation Constants

$\log \beta^{H}_{J}$	$\log \beta^{H}_{1}$	$\log \beta^{H}_{2}$	$\log \beta^{H}_{3}$	$\log \beta^{H}_{4}$	$\log \beta^{H}_{5}$	$\log \beta^{H}_{6}$
graphical values	9.70 ± 0.03	18.70 ± 0.04	23.07 ± 0.04	25.79 ± 0.05	28.39 ± 0.05	30.30 ± 0.05
refined values	9.74 ± 0.01	18.38 ± 0.01	23.16 ± 0.01	26.06 ± 0.01	28.40 ± 0.02	30.55 ± 0.02

approach.[16] Accordingly, it was possible to draw a simple starting model, to be refined through an iterative procedure.[17]

Protonation Constants. The six overall protonation constants of the ligand, related to the generic equilibrium (eq 16), with $1 < j < 6$, and defined as in eq 17, have been obtained from the treatment of experimental data collected on solutions S_L in the absence of metal cations.

$$jH^+ + A^{5-} \rightleftarrows H_jA^{j-5} \tag{16}$$

$$\beta_j^{H} = \frac{[H_jA^{j-5}]}{[H^+]^j \cdot [A^{5-}]} \tag{17}$$

The protonation curve reported in Figure 3 represents the trend, against $-\log h$, of the secondary variable $\bar{n}$, the average number of protons bound to the ligand, defined as:

$$\bar{n} = \frac{\sum_{j=0}^{n} j \cdot [H_jA]}{\sum_{j=0}^{n} [H_jA]} \tag{18}$$

It results from the ratio of the total concentration of H^+ ions bound to the ligand, to the total ligand concentration A:

$$A = \sum_{j=0}^{n} [H_jA] \tag{19}$$

According to the usual procedures,[16,18] $\bar{n}$ can be calculated from experimental data, by means of eq 20:

$$\bar{n} = \frac{H - h + [OH^-]}{A} \tag{20}$$

where the term H represents the total concentration of H^+ ions (bound and free) in solution, which can be easily calculated from primary data:

$$H = H^\circ + 5A - C_b + H_T \tag{21}$$

Here H° represents the $HClO_4$ concentration in solution S_L, A that of the ligand, C_b that of the electrochemically generated OH^- ions, and H_T the concentration of $HClO_4$ added in the back-titration with solution T°.

The form of the protonation curve reported in Figure 3 gives some useful clues on the ligand behavior in the ionic medium used:

(i) As the form and the position of the protonation curve is independent from the total ligand concentration, no polynuclear species are present in the concentration range investigated $[(3 \cdot 10^{-3} \text{ to } 13 \cdot 10^{-3})\ m]$;

(ii) As the curve shows only one horizontal trait at $\bar{n} = 2$, in the acidity range $5 < -\log h < 8$, we can conclude that, apart from H_2A^{3-}, no single species predominates in any pH range;

(iii) As at the lower $-\log h$ values, the curve does not flatten at $n = 5$, we can infer that, due to the presence of three nitrogen atoms each bearing an electron lone pair, the H_5A molecule can react as a base binding further protons to a maximum of three.[19]

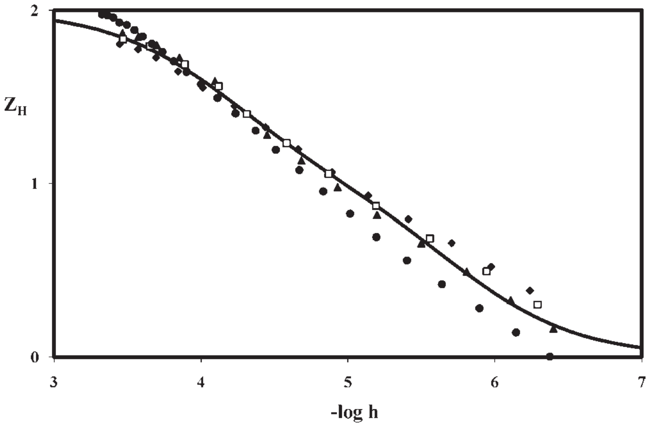

Figure 4. Protonation curve of the complexes. ●, $0.61 \cdot 10^{-3}$ m; ▲, $1.6 \cdot 10^{-3}$ m; □, $2.0 \cdot 10^{-3}$ m; ♦, $3.2 \cdot 10^{-3}$ m; —, best fit curve.

These considerations suggest the hypothesis that six protonated species can exist in our solutions; a graphical approach[18] to linearize primary data gave preliminary values of the six stability constants, which were then refined, as reported in the following. On the first line of Table 1 are reported values obtained by a graphical method, on the second line the refined ones.

Complex Formation Equilibria. To determine the correct composition of solutions containing equal amounts of uranyl ions and of the ligand DTPA is quite a difficult task. Almost three kinds of equilibria can take place in these solutions: hydrolysis equilibria involving the uranyl ion giving species of generic formula $[(UO_2)_q(OH)_i]^{(2q-i)+}$; acid−base equilibria involving ligand species of generic formula $[H_jA]^{(j-5)+}$; complex formation equilibria leading to species of generic formula $[(UO_2)_qA_n]^{(2q-5n)+}$, which can further react with the solvent water to give protonated $[H_p(UO_2)_qA_n]^{(p+2q-5n)}$ or deprotonated $[(UO_2)_qA_n(OH)_p]^{(2q-5n-p)}$ species.

As a consequence, no simple graphical approach could be used without introducing gross simplifications, for instance assuming that the high stability of complex species with DTPA makes negligible the presence of weak complexes.

The average number Z_H of protons bound to the complex could be calculated from data collected in solutions S_{ML}, by means of eq 22 and plotted against $-\log h$ in Figure 4:

$$Z_H = \frac{H - h + [OH^-]}{A} \tag{22}$$

As the experimental data crowd around a single curve, one can infer that, in the concentration range investigated (A and B varied between $(1.2 \text{ and } 5.7) \cdot 10^{-3}$ m), only mononuclear complex species, with a and p equal to 1, were formed. As shown in Figure 4, where data from three different titrations are reported, Z_H values range between 2 and 0, according to the smooth

Table 2. Preliminary Values of the Complex Acidity Constants

$\log K_1$	$\log K_2$	$\log K_{-1}$
-4.20 ± 0.07	-5.8 ± 0.3	-7.6 ± 0.3

Table 3. Comparison between Seven and Six Species Models

	χ^2	σ^2
Model I (seven species)	11.49	0.9098
Model II (six species)	13.52	2.1852

increase of $-\log h$ between $\varphi = 3$ and $\varphi = 5$, in the titration curve of the complex. This suggests, as a starting guess, that the only complex species were $[H_2MA]^-$, $[HMA]^{2-}$, and $[MA]^{3-}$.

$$H_2MA^- \rightleftarrows HMA^{2-} + H^+ \tag{23}$$

$$HMA^{2-} \rightleftarrows MA^{3-} + H^+ \tag{24}$$

Moreover, the absence of an asymptotic convergence of the curve to $Z_H = 0$ suggests the possibility of a hydrolyzed complex species, according to:

$$MA^{3-} + H_2O \rightleftarrows [MAOH]^{4-} + H^+ \tag{25}$$

A preliminary graphic treatment[18] of data gave the values of the complexes acidity constants defined as reported in eq 26 and reported in Table 2:

$$K_1 = \frac{h \cdot [HMA^{2-}]}{[H_2MA^-]}$$

$$K_2 = \frac{h \cdot [MA^{3-}]}{[HMA^{2-}]} \qquad K_{-1} = \frac{h \cdot [MAOH^{4-}]}{[MA^{3-}]} \tag{26}$$

Data Refinement. Experimental data gathered in titrations of solutions S_L and S_{ML} have been separately treated by means of the refinement suite of programs HYPERQUAD.[20] They require the input of a model file and of a potentiometric data file. The model file consists of a set of chemical species and of their stability constants, which must be refined, and parameters which must be kept constant, as, for instance, the ionic product of water if it has been previously determined in the ionic medium used. The data file contains primary data in the form (t, E).

The HYPERQUAD output file contains the values of the refined stability constants which best fit the experimental data and two additional statistical parameters, σ^2 and χ^2, which allow evaluation of the quality of the result. The former, σ^2, is the sample variance of the weighted fit; its value, in absence of systematic errors, is very near unity. Anyway, in the pessimistic hypothesis that the experimental error is three times the expected one, $\sigma^2_{\lim} = 9$ can be taken as a significance limit for this parameter.[20] The latter, χ^2, results from the analysis of the residual distribution and shows the existence of systematic errors, such evaluating the goodness of the proposed model. If χ^2 is lower than the limiting value of 12.6, the experimental errors have a Gaussian distribution at the 95 % confidence level.

Protonation Constants. To obtain refined values of the ligand protonation constants, we introduced in HYPERQUAD two different models. Model I consisted of the seven species from H_6A^+ to A^{5-} and the preliminary values of their overall protonation constants, from $\beta^H{}_1$ to $\beta^H{}_6$, reported in Table 1. Model II was obtained by dropping away H_6A^+, leaving only six species, from H_5A to A^{5-}. The refinement process on the two different input models gave the statistical parameters reported in Table 3.

Table 4. Overall Formation Constants for the Uranyl-DTPA Complexes in 3 M $NaClO_4$ at 25 °C

qnp	110	111	112	11−1
$\log \beta_{qnp}$	13.63 ± 0.02	19.77 ± 0.02	23.85 ± 0.02	4.8 ± 0.1
formula	$[UO_2A]^{3-}$	$[HUO_2A]^{2-}$	$[H_2UO_2A]^-$	$[UO_2A(OH)]^{4-}$

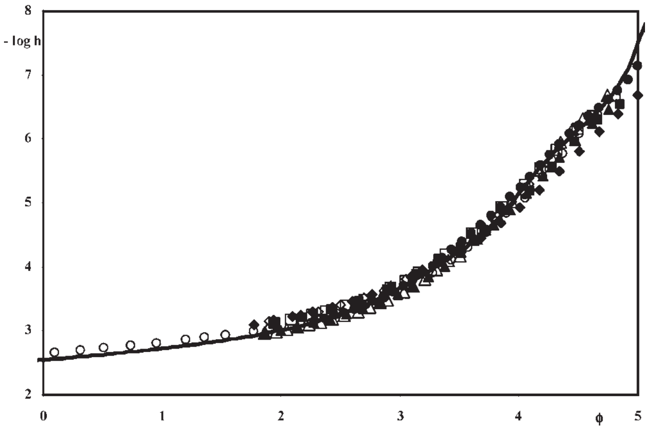

Figure 5. Best fit of the titration curves. Empty dots refers to volumetric titrations, full dots to electrochemical back-titrations; △, $B = 5.5 \cdot 10^{-3}$ m; ▲, $B = 3.2 \cdot 10^{-3}$ m; ■, $B = 2.1 \cdot 10^{-3}$ m; □, $B = 2.6 \cdot 10^{-3}$ m; ♢, $1.9 \cdot 10^{-3}$ m; ♦, $B = 1.6 \cdot 10^{-3}$ m; ●, $B = 3.1 \cdot 10^{-3}$ m; ○, $B = 3.0 \cdot 10^{-3}$ m; —, best fit curve.

As can be seen, the statistical parameters of model I lie below the critical values and exclude systematic errors; on the contrary, by eliminating the species H_6A^+, the σ^2 and χ^2 values show that a systematic error has been introduced in model II. In Figure 3, the two curves show the differences between the two models and the better agreement of the experimental data with model I.

In Table 1, refined values of the overall protonation constants are reported, showing a good agreement with those obtained from the graphical treatment of data.

Complex Formation Constants. The starting model introduced into the program contained the complex species $[MA]^{3-}$, $[HMA]^{2-}$, $[H_2MA]^-$, $[MAOH]^{4-}$, and the preliminary values of their formation constants. As fixed parameters, we introduced the ionic product of water, the ligand protonation constants (determined as above) and the uranyl ion hydrolysis constants, determined from Manfredi et al.,[5] in the same ionic medium.

The best values of the overall stability constants, referring to the generic equilibrium (eq 27) and defined as in eq 28, are reported in Table 4.

$$pH^+ + qM^{2+} + nA^{5-} \rightleftarrows H_pM_qA_n{}^{(2q+p-5n)+} \tag{27}$$

$$\beta_{qnp} = \frac{[H_pM_qA_n{}^{(2q+p-5n)+}]}{[M^{2+}]^q \cdot [A^{5-}]^n \cdot [H^+]^p} \tag{28}$$

The related statistical parameters were below the limiting values: χ^2 was 9.30, confirming a Gaussian distribution of errors, at a

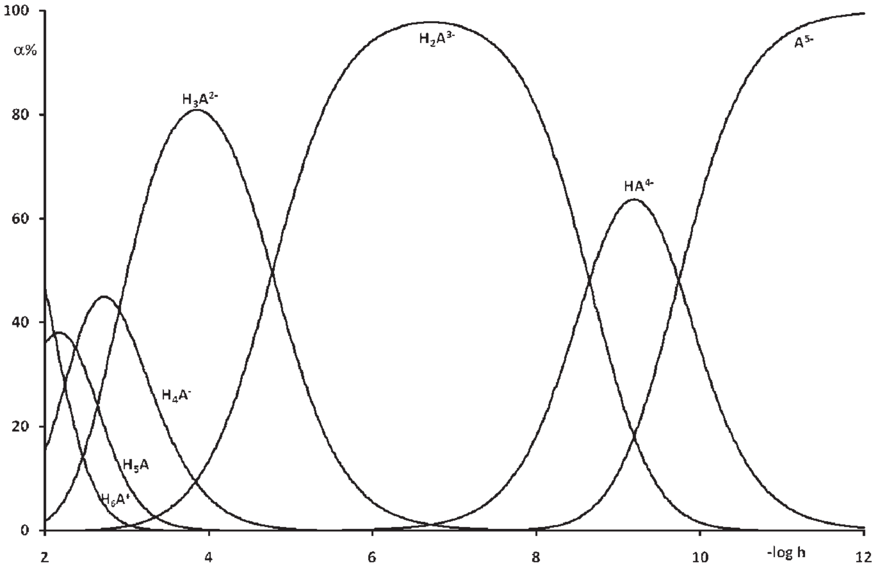

Figure 6. Distribution diagram of species from deprotonation of DTPA.

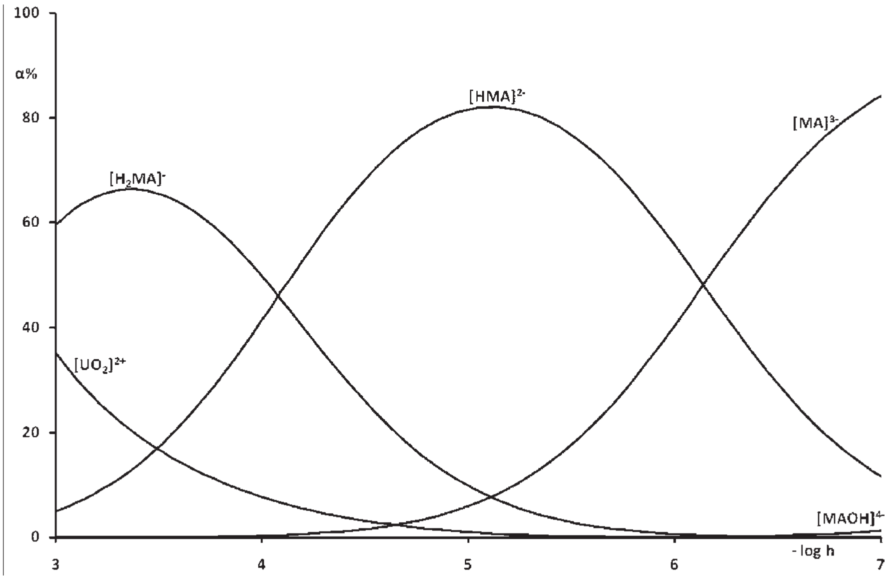

Figure 7. Distribution curves of complexes.

confidence level of 95 %, while σ^2 was 8.74, still below the accepted limiting value of 9.[20]

The chosen model has the further advantage of being extremely simple, as it contains only monomeric species. As a further check, we tested with HYPERQUAD some alternative models, by adding some dimeric species. Statistical parameters get worse, showing that a systematic error had been introduced with the additional species. The only species whose introduction left almost unchanged the statistical parameters was the dimer of formula $[HM_2A]$, but its stability constant ($\log \beta_{211} = 22.53$) showed an excessive standard deviation (more than 33 % its value). Anyway, the introduction of this species did not appreciably change the distribution curve of the complex species. On the other hand, any attempt to prepare solutions having metal-to-ligand ratios different from 1:1 gave rise to slight soluble species, which slowly dissolved only when the proper 1:1 ratio was restored.

Moreover, as it was impossible to obtain data at higher values of $-\log h$, owing to insoluble product formation, the nature of hydroxyl species could not be better investigated.

In Figure 5 experimental points obtained in four different titrations and back-titrations are compared with the titration curve calculated on the basis of the constant values reported in Table 4.

In Figure 6, the distribution curves of the different protonated species are reported against $-\log h$; the diprotic species $[H_2A]^{3-}$ shows a wider predominance range, from $-\log h = 5$ to $-\log h = 8$.

The addition of uranyl ions caused the formation of complex species. Graphical and statistic refinements of data allowed us to recognize four complex species, whose distribution curves are reported in Figure 7, for a solution in which the ligand and the cation concentrations are equal to $3 \cdot 10^{-3}$ *m*.

The stability of the complex $[MA]^{3-}$ can be ascribed to the good chelating properties of the $DTPA^{5-}$ anion toward large

Table 5. Comparison between Stability Constants of the Complexes

qnp	110	111	112	113	210	11−1	
log β_{qnp}	14.0	19.50	23.65	27.10	19.50		values from ref 25
log β_{qnp}	13.63	19.77	23.85	-	-	4.85	this work

cations;[21] likely, the particular form of the uranyl ion, with the two oxygen atoms in apical positions, affects the number and the position of the coordination sites. As a consequence, polydentate ligands can coordinate uranyl only in the equatorial plane. Owing to its size, DTPA can achieve complete tetracoordination, involving both its aminodicarboxylic groups at the ends of the molecule. This should improve the stability of the mononuclear complexes and prevent the formation of mononuclear hydroxo species.[22]

On the other hand, the smaller size of ethyenediaminetetraacetic acid (EDTA) does not allow coordination of uranyl with two amino dicarboxylic groups, so favoring both the hydroxo complexes formation, both the coordination of two uranyl ions with only one EDTA ion;[23,24] this 1:2 ratio is quite unusual for EDTA complexes.

The formation of the DTPA complexes saturates all of the coordination sites of uranyl, thus preventing the formation of hydroxo species; anyway, in more alkaline solutions this is more difficult to realize, and a small contribution from hydroxylated complexes is found. In these conditions, coordination sites of uranyl are occupied by hydroxo ions, and the formation of polynuclear species can be favored to a small extent.[25]

In Table 5 our results are compared with those obtained by Bucci et al.,[25] the only one reported in sodium perchlorate medium (first line: values from ref 25, ionic medium 1 M $NaClO_4$ at 20 °C; second line: this work). Despite this difference and the different procedures of data collection, good agreement can be observed.

CONCLUSION

The joined use of electrochemical and volumetric titrations allowed us to collect a great number of experimental data, by means of a potentiometric cell containing a glass electrode.

The coulometric generation of OH^- ions offers several advantages: it allows one to avoid long and delicate procedures of preparation, standardization, and storage of alkali solutions, and it is free from significant amounts of impurities, which could interfere with the investigated acid−base equilibria. Moreover, no variation of volume, and hence of the ionic strength of the solution, occurs.

So we could characterize aqueous solutions of H_5DTPA, both with or without uranyl ions, at 25 °C in 3 M $NaClO_4$.

We could ascertain that, in the acidity range $2 < -\log h < 12$, when the total ligand concentration is lower than 0.015 *m*, the ligand undergoes six protonation equilibria.

In conclusion, we believe that the experimental procedure we proposed allowed us to gather abundant and consistent experimental data which, together with the refinement method used, guarantee the reliability of our results.

As can be seen in Figure 7, complex species largely predominate in the investigated solutions, preventing the formation of slightly soluble hydroxo species and maintaining uranyl ion in solution until $-\log h = 7$. These results suggest, for instance, that it is possible to use neutral solutions to leach uranyl ions from solids.

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