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Interactions of Dioxouranium(VI) with Polyamines in Aqueous Solution

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The interaction of the dioxouranium(VI) ion with five low molecular weight polyamines (ethylenediamine, putrescine, cadaverine, spermidine, and spermine) and with poly(allyl)amine (15 kDa) was studied potentiometrically (ISE-H^+ glass electrode) at $T = 298.15$ K. Investigations were carried out in $NaNO_3$ ionic medium, at $I = 0.1\ mol\cdot L^{-1}$ (and $0.5\ mol\cdot L^{-1}$ for poly(allyl)amine only), in the pH range 3.5 to 5.5, before the formation of uranyl insoluble species. The results gave evidence for the formation of two species, namely, UO_2L^{2+} and $UO_2L(OH)^+$ for the diamine systems (ethylenediamine, putrescine, cadaverine), UO_2L^{2+} and UO_2LH^{3+} for spermidine, and UO_2LH^{3+} and $UO_2LH_2{}^{4+}$ for spermine. In the system UO_2−poly(allyl)amine, four species, namely, UO_2L^{2+}, UO_2LH^{3+}, $UO_2LH_2{}^{4+}$, and $UO_2L(OH)^+$, are formed. Speciation profiles of the different systems and the sequestration capability of amines at various pH values are discussed. Some empirical relationships regarding the formation constants of complex species are also reported.

Introduction

Among radionuclides, uranium is the most investigated owing to its large use in several civilian and military application fields.[1–7] As is well-known, in aquatic ecosystems uranium(VI) is present mainly as dioxouranium species ($UO_2{}^{2+}$, uranyl) which shows radiological and health effects[8–12] lower than those of elemental uranium. On the contrary, uranyl shows a very high reactivity in aqueous solution as documented by several articles and compilations.[13–19] In the past decade, we have carried out a systematic study on the hydrolysis and on the interaction of the uranyl ion with different ligands in various ionic media and at different ionic strengths.[20–33] In particular, we focused our attention on $UO_2{}^{2+}$ complexation with ligands of biological and environmental interest such as carboxylic acids,[23–29] amino acids (including complexones),[30,31] nucleotides,[32] and fulvic and alginic acids (work in preparation). As an extension of our previous studies, we report here the results of an investigation on the interaction of uranyl with N-donor ligands. Amino groups are present in many substances of biological and environmental interest such as amino acids and proteins, nucleic acids, biogenic amines, humic substances, chitin and its derivatives, and so forth. Amines are widespread, as trace components, in several natural and biological fluids (blood, urine, saliva, and natural waters) and in various other natural matrices (vegetables, fruits, and many fermented foods and beverages) where biogenic amines can be easily formed.[34]

According to Cassol et al.,[35] the N-donor ligands, owing to their high basicity, tend in aqueous solution to bind protons preferentially instead of $UO_2{}^{2+}$ ions, and it may be difficult to obtain quantitative data on the formation of complex species between the uranyl ion and the amines. On the other hand, different considerations can be made on the basis of results obtained in a previous study concerning the interaction of the uranyl ion with amino acids.[30] In that work, by comparing the stability of $UO_2{}^{2+}$−aspartate and $UO_2{}^{2+}$−malonate complex species (at $I = 0.1\ mol\cdot L^{-1}$ (NaCl) and $T = 298.15$ K), a significantly higher stability of the $UO_2{}^{2+}$−aspartate species ($\log \beta = 7.58$) with respect to that of the analogous $UO_2{}^{2+}$−malonate species ($\log \beta = 5.71$) was found. Since both of the ligands present two carboxylic groups and differ only by the presence of one amino group in the aspartate, the higher stability (about 1.9 log units) of the UO_2−aspartate system must be evidently attributed to further interaction of the uranyl ion with the amino group, in addition to the well-established interaction with carboxylic binding sites.[23–29]

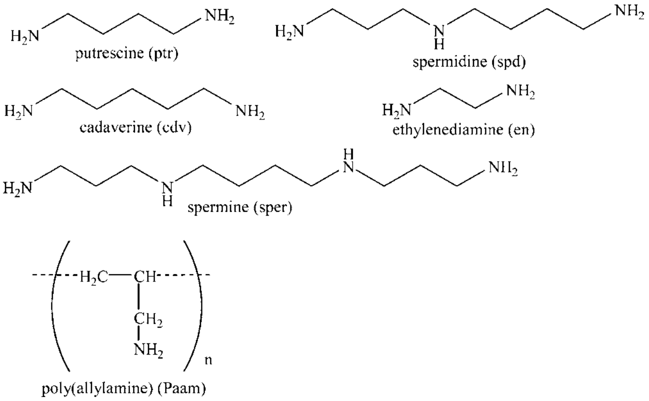

Figure 1. Schematic structure of amines considered in this work.

In the light of the above considerations, we planned the present study on the interaction of $UO_2{}^{2+}$ with different amines, including some biogenic amines, (i) to define the stability of the complex species formed and (ii) to evaluate the contribution of amino groups to the stability of $UO_2{}^{2+}$ complexes with ligands containing both −O and −N potential binding sites, as for example, amino acids, humic substances, and so forth. In particular the following amines were considered (structures in Figure 1): ethylenediamine (1,2-diamino-ethane, en), putrescine

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(1,4-diamino-butane, ptr); cadaverine (1,5-diamino-pentane, cdv); spermidine (*N*-(3-aminopropyl)-1,4-diamino-butane, spd); and spermine (*N*,*N*′-bis(3-aminopropyl)-1,4-diaminobutane), sper); moreover, the interaction of $\mathrm{UO_2}^{2+}$ with poly(allyl)amine (paam), an ammonium polyelectrolyte (with a 15 kDa average molecular weight), was investigated to compare the stability of uranyl complexes with low and high molecular weight amino ligands.

Investigations were carried out by potentiometry (ISE-H^+ glass electrode) in $\mathrm{NaNO_3}$ ionic medium at 0.1 $\mathrm{mol \cdot L^{-1}}$ ionic strength (and also at 0.5 $\mathrm{mol \cdot L^{-1}}$ for the $\mathrm{UO_2}$−paam system) and at $T = 298.15$ K.

Experimental Section

Chemicals. The dioxouranium(VI) cation ($\mathrm{UO_2}^{2+}$) was used as the nitrate salt (Fluka), whose purity, checked gravimetrically after precipitation as $\mathrm{U_3O_8}$ by gaseous ammonia was > 99.5 %. The amines (by Fluka) were used in their hydrochloride form. Their purity, checked alkalimetrically, was always > 99.5 %. Nitric acid and sodium hydroxide solutions were prepared by diluting concentrated ampules (Fluka) and were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. Sodium nitrate solution was prepared by weighing pure salt (Fluka) previously dried in an oven at 383.15 K. All of the solutions were prepared using analytical grade water ($R \geq 18$ MΩ) and grade A glassware.

Apparatus and Procedure. Potentiometric titrations were carried out at $T = (298.15 \pm 0.1)$ K using an apparatus consisting of a model 665 Metrohm motorized buret coupled with a model 713 Metrohm potentiometer equipped with a combined glass electrode (Ross type 8172, from Orion). The estimated accuracy was ± 0.15 mV and ± 0.003 mL for emf and titrant volume readings, respectively. The apparatus was connected to a personal computer, and automatic titrations were performed using a suitable computer program to control titrant delivery and data acquisition and to check for emf stability. All titrations were carried out under magnetic stirring and bubbling purified, presaturated $\mathrm{N_2}$ through the solution to exclude $\mathrm{O_2}$ and $\mathrm{CO_2}$. The measurements for protonation constants were carried out in an initial volume of 25 mL of solution containing the amine hydrochloride under study ($1.3 \leq C_\mathrm{L}/\mathrm{mmol \cdot L^{-1}} \leq 10$) and $\mathrm{NaNO_3}$, added to obtain pre-established ionic strength value ($I = 0.1$ $\mathrm{mol \cdot L^{-1}}$ and $I = 0.5$ $\mathrm{mol \cdot L^{-1}}$ for the paam system only); the solutions were titrated with standard NaOH up to (80 to 90) % neutralization in the pH range 5.5 to 11, and for each experimental condition, at least 6 runs were performed. The measurements for the determination of $\mathrm{UO_2}$−amine complex formation constants were carried out over a wide range of component concentrations and at ligand/metal molar ratios up to ∼ 3:1. The experimental conditions used are $1.0 \leq C_\mathrm{UO2}/\mathrm{mmol \cdot L^{-1}} \leq 5.1$ and $2.7 \leq C_\mathrm{L}/\mathrm{mmol \cdot L^{-1}} \leq 11.7$; for each experimental condition five to seven runs were made, and as in the case of the measurements for protonation constants, about 600 points were collected. To determine the formal electrode potential for each experiment, independent titrations of $\mathrm{HNO_3}$ with NaOH standard solutions were carried out, in the same experimental conditions of ionic strength and temperature as the systems under study.

Calculations. The nonlinear least-squares computer program ESAB2M[36] was used to determine all of the parameters of the acid−base potentiometric titrations (reagents concentration, formal potential of electrode, junction potential coefficient, ionic product of water K_w). The protonation constants of the amines and the formation constants of the dioxouranium(VI)−amine complexes were refined using the STACO and BSTAC computer programs.[37] The ES4ECI computer program[37] was used to obtain distribution diagrams of the species in solution (speciation profiles) and to compute percentage formation of the species. All of the formation constants are expressed according to the equilibria

$$p\mathrm{UO_2}^{2+} + q\mathrm{L}^0 + r\mathrm{H}^+ = (\mathrm{UO_2})_p(\mathrm{L})_q\mathrm{H}_r^{(2p+r)} \quad (\beta_{pqr}) \tag{1}$$

$$p\mathrm{UO_2}^{2+} + q\mathrm{LH}_r^{r+} = (\mathrm{UO_2})_p(\mathrm{L})_q\mathrm{H}_r^{(2p+r)} \quad (K_{pqr}) \tag{1a}$$

$$p\mathrm{UO_2(OH)}_r^{(2p-r)} + q\mathrm{L} = (\mathrm{UO_2})_p(\mathrm{L})_q(\mathrm{OH})_r^{(2p-r)} \quad (K_{pqr}) \tag{1b}$$

where L represents the amines considered in this work.

Table 1. Hydrolysis Constants of Uranyl Ion in $\mathrm{NaNO_3(aq)}$, at $I = 0.1$ $\mathrm{mol \cdot L^{-1}}$ and at $T = 298.15$ K

hydrolysis equilibrium	$-\log \beta^a$
$\mathrm{UO_2}^{2+} + \mathrm{H_2O} = (\mathrm{UO_2})(\mathrm{OH})^+ + \mathrm{H}^+$	5.38
$2\mathrm{UO_2}^{2+} + 2\mathrm{H_2O} = (\mathrm{UO_2})_2(\mathrm{OH})_2{}^{2+} + 2\mathrm{H}^+$	5.98
$3\mathrm{UO_2}^{2+} + 4\mathrm{H_2O} = (\mathrm{UO_2})_3(\mathrm{OH})_4{}^{2+} + 4\mathrm{H}^+$	12.29
$3\mathrm{UO_2}^{2+} + 5\mathrm{H_2O} = (\mathrm{UO_2})_3(\mathrm{OH})_5{}^{+} + 5\mathrm{H}^+$	16.52
$3\mathrm{UO_2}^{2+} + 7\mathrm{H_2O} = (\mathrm{UO_2})_3(\mathrm{OH})_7{}^{-} + 7\mathrm{H}^+$	29.57

[a] Ref 20.

Results and Discussion

Protonation of Amines and Hydrolysis of Dioxouranium(VI). The complexation models for the different $\mathrm{UO_2}$−amine systems were obtained by taking into account both the hydrolysis of the uranyl(VI) ion and the protonation of amines in the same ionic medium and at the same ionic strength. The hydrolysis of the uranyl ion has been widely studied in different experimental conditions, and the hydrolysis constant values can be found in many articles and compilations.[13–22] The hydrolysis constants we used here for $\mathrm{UO_2}^{2+}$ in $\mathrm{NaNO_3}$ ionic medium, at $I = 0.1$ $\mathrm{mol \cdot L^{-1}}$,[20] are reported in Table 1.

Though the acid−base properties of the low molecular weight polyamines considered here (en, ptr, cdv, spd, sper) have been extensively investigated,[15–19,38,39] their protonation constants are not reported in the literature at the ionic strength (0.1 $\mathrm{mol \cdot L^{-1}}$) and medium ($\mathrm{NaNO_3}$) conditions considered here. For this reason we carried out experimental measurements to determine protonation constants for all of the amines investigated, including poly(allyl)amine, at the desired ionic strength and medium. For poly(allyl)amine the ionic strength of 0.5 $\mathrm{mol \cdot L^{-1}}$ ($\mathrm{NaNO_3}$) was also considered to check the influence of ionic medium on the acid−base and complexation properties (see here after Section , Complex Species Formation). The values of protonation constants for all polyamines investigated are reported in Table 2.

As can be seen, the acid−base properties of poly(allyl)amine are expressed by two protonation constants, and this deserves a short digression. In fact, the acid−base properties of this ligand, like that of every polyelectrolyte, cannot be studied with the classical approach used for a low molecular weight ligand. Different models were proposed in the literature to study the acid−base behavior of polyelectrolytes, such as the modified Henderson−Hasselbalch equation, first proposed by Katchalsky,[40] and the three-parameter model proposed by Högfeldt et al.[41] In both of these models the protonation constants of the polyelectrolytes are a continuous function of the dissociation

Table 2. Protonation Constants[a] of Amines in $NaNO_3$, at $T = 298.15$ K

polyamines	$\frac{I}{\mathrm{mol \cdot L^{-1}}}$	$\log \beta_{011}$[a]	$\log \beta_{012}$[a]	$\log \beta_{013}$[a]	$\log \beta_{014}$[a]
en	0.1	9.907 ± 0.003[b]	17.023 ± 0.004[b]		
ptr	0.1	10.833 ± 0.003	20.339 ± 0.003		
cdv	0.1	10.907 ± 0.003	20.807 ± 0.003		
spd	0.1	10.883 ± 0.003	20.710 ± 0.001	29.069 ± 0.005[b]	
sper	0.1	10.907 ± 0.006	20.914 ± 0.003	29.765 ± 0.007	37.743 ± 0.010 [b]
paam	0.1	9.623 ± 0.015	17.590 ± 0.018		
paam	0.5	9.793 ± 0.013	18.146 ± 0.016		

[a] Refers to the equilibrium (1). [b] Uncertainty limits are 95 % confidence intervals.

Table 3. Formation Constants[a,b] of Complex Species in the Systems UO_2−Amines in $NaNO_3$(aq), at $I = 0.1$ mol·L^{-1} and at $T = 298.15$ K

amine	$\log \beta_{112}$[a]	$\log \beta_{111}$[a]	$\log \beta_{110}$[a]	$\log \beta_{11\text{-}1}$[a]
en			9.88 ± 0.10[c]	3.21 ± 0.05[c]
ptr			13.07 ± 0.03	7.10 ± 0.05
cdv			12.20 ± 0.12	6.38 ± 0.10
spd		21.60 ± 0.03[c]	15.11 ± 0.6	
sper	29.87 ± 0.06[c]	24.42 ± 0.03		
paam	21.80 ± 0.04	17.40 ± 0.03	12.87 ± 0.04	7.16 ± 0.05
paam ($I = 0.5$ mol·L^{-1})	22.38 ± 0.05	18.20 ± 0.05	13.58 ± 0.15	7.98 ± 0.06
	$\log K_{112}$[b]	$\log K_{111}$[b]	$\log K_{110}$[b]	$\log K_{11\text{-}1}$[d]
en			9.88	8.59
ptr			13.07	12.48
cdv			12.20	11.76
spd		10.72	15.11	
sper	8.95	13.51		
paam	4.21	7.78	12.87	12.54
paam ($I = 0.5$ mol·L^{-1})	4.24	8.41	13.58	13.39

[a] $\log \beta_{pqr}$ refers to the equilibrium (1). [b] $\log K_{pqr}$ refers to the equilibria (1a). [c] Uncertainty limits are 95 % confidence intervals. [d] $\log K_{pqr}$ refers to the equilibria (1b).

degree α of the macromolecule. Recently we adopted a new model[42,43] according to which the protonation of a polyelectrolyte is independent of its dissociation degree and can be expressed by means of two protonation constants only corresponding to a diprotic behavior of the monomeric unit of the polyelectrolyte ("diprotic-like model"). The results obtained using this model in a recent study on the acid−base properties of eleven natural and nine synthetic polyelectrolytes[42] show that there is a negligible loss of precision in comparison with the classical Henderson−Hasselbalch and Högfeldt models, and therefore, it can be used successfully like these cited models. Using the "diprotic-like model", we calculated, from the experimental data obtained here, the protonation constants of poly(allyl)amine in $NaNO_3$ at (0.1 and 0.5) mol·L^{-1} ionic strengths. The values are reported in Table 2. Protonation constants of poly(allyl)amine were studied at different ionic strengths in NaCl and LiCl aqueous solution,[44] and the protonation constant values are in accordance with those found here.

Complex Species Formation in the Uranyl−Amine Systems. Calculations performed on the experimental potentiometric data, at $I = 0.1$ mol·L^{-1} ($NaNO_3$) and $T = 298.15$ K, gave evidence for the formation of the following complex species: UO_2L^{2+} and $UO_2L(OH)^+$ in the UO_2−en, −cdv, and −ptr (diamine) systems; UO_2L^{2+} and UO_2LH^{3+} and UO_2LH^{3+} and $UO_2LH_2^{4+}$ in UO_2−spd (triamine) and UO_2−sper (tetramine) systems, respectively. Poly(allyl)amine forms four species, namely, UO_2L^{2+}, UO_2LH^{3+}, $UO_2LH_2^{4+}$, and $UO_2L(OH)^+$. These speciation models were chosen, among other possible models, on the basis of the following selection criteria:[45] (i) the analysis of ratios between single variances and that of the accepted model (ratios were considered significant at 95 % confidence interval), (ii) the simplicity of the model (the addition of other minor species renders the model unrealistically complicated), and (iii) the likelihood of the proposed species, and (iv) as a further check, during calculations, we also refined some of UO_2 hydrolytic species without sensibly altering the values of UO_2−amine complex formation constants. These and other criteria for model selection were discussed in ref 46. As can be seen, the species considered in the selected speciation models are strongly positively charged, and in the presence of an excess of an anion in solution, in this case NO_3^-, a further interaction can occur influencing their stability. To verify this hypothesis we carried out, for the UO_2−paam system, in addition to measurements performed at $I = 0.1$ mol·L^{-1}, measurements at $I = 0.5$ mol·L^{-1} in $NaNO_3$ medium. The overall (eq 1) and partial (eq 1a) formation constants of the species formed in all of the systems investigated are reported in Table 3. As can be seen, the stability of uranyl−amine complexes is quite high, in particular for the unprotonated species. Moreover, for the UO_2^{2+}−paam system we notice that the species UO_2L^{2+}, UO_2LH^{3+}, and $UO_2L(OH)^+$ show at $I = 0.5$ mol·L^{-1} a stability much higher than those at $I = 0.1$ mol·L^{-1}, while for the diprotonated complex species the stability is almost the same at the two ionic strengths. This behavior can be explained by hypothesizing a stabilization of the cationic species by the anion of the supporting electrolyte. This trend is not respected for the $UO_2LH_2^{4+}$ species, for which the repulsive effect of the reactants prevails: in fact, the stabilizing effect due to the interaction with the anion of the supporting electrolyte increases with the positive charge of the cationic complex, while the repulsive effect between the reactants increases with the product of their positive charges. An analogous effect was observed in the UO_2^{2+}−oxalate system[25] whose anionic complexes are significantly stabilized by Na^+ of the supporting electrolyte.

By analyzing the formation constants reported in Table 3, we can make the following considerations: (a) for diamines, very different stabilities are observed (> 3 log units) as a function of the distance between the two amino groups in the molecules;

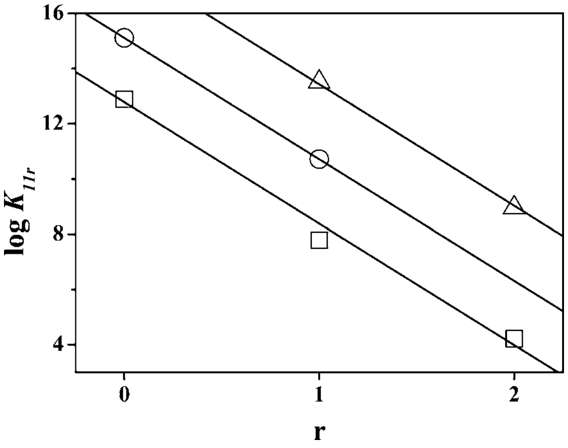

Figure 2. Dependence of formation constants of poly(allyl)amine−, spermidine−, and spermine−uranyl complex species on the number of protons *r*. Symbols. ○, spd; □, paam; △, sper.

(b) the stability of the complex species depends, as expected, on the number of amino groups involved in the coordination (the unprotonated ones); (c) as a consequence of the last consideration, the difference in the stability of unprotonated and hydroxo-species is very low and fairly constant for poly(allyl)amine, putrescine, and cadaverine; (d) the stability of protonated species decreases systematically for spermine, spermidine, and poly(allyl)amine and is ≤ 4 log units for each added proton.

Empirical Relationships. Thermodynamic parameters (such as stability constants, entropies, enthalpies) regarding the formation of any species certainly depends on the experimental conditions (ionic medium, ionic strength, temperature, etc.) adopted in the experiments. Moreover, if we consider the species formed by ligands belonging to an homologous series (in this case amines) with a metal ion (in this case UO_2^{2+}) and we fix the experimental conditions mentioned above, a significant dependence can also be found of the same thermodynamic parameters on some characteristics of the ligands structure, that can be very useful for predictive purposes.

In this case, two important empirical correlations were found. The first one regards the dependence of log *K* for the following: (i) the number of functional groups involved in the coordination, that is, the amino groups unprotonated, n_N; (ii) the mean distance between them in the molecule *d* (calculated as the number of terms of chelate ring(s), but the cation); and (iii) the number of −OH groups bound to UO_2^{2+} n_{OH}:

$$\log K(\pm 0.5) = p_1 n_N + p_2(d - 6)^2 + p_3 n_{OH} \tag{3}$$

with $p_1 = 5.8$, $p_2 = -0.44$, and $p_3 = -0.40$. The second correlation regards the trend reported in point (d) of the previous section that can be expressed by a simple linear equation:

$$\log K_{11r} = \log K_{110} + Ar \tag{4}$$

with r = number of protons in the complex species. The empirical parameter *A* is very similar for all the protonated species, so we constrained the value of *A* to be equal to $A = -4.40 \pm 0.06$. As can be seen in Figure 2, the three straight lines are almost perfectly parallel. Extrapolated values of log K_{110} are 12.8 ± 0.1, 15.1 ± 0.1, and 17.8 ± 0.2 for poly(allyl)amine, spermidine, and spermine, respectively. In other words, the decreasing effect is independent of the overall stability and of the type of amine considered. This also allows calculation of the formation constant of $M_pL_qH_r$ species for systems in which precipitation renders impossible the experimental determination of that constant, as in the case of spermine.

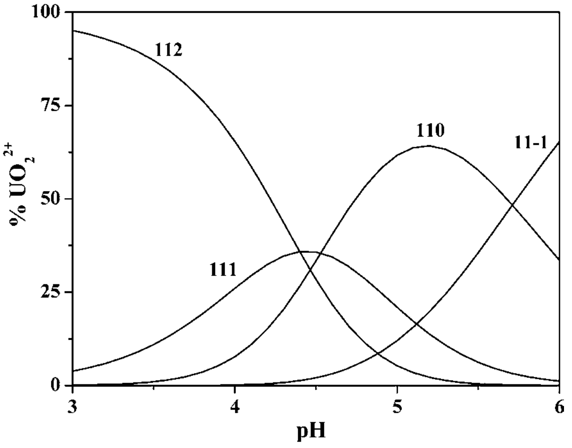

Figure 3. Distribution of species vs pH in the system UO_2^{2+}−paam, in $NaNO_3$ ionic medium and at $T = 298.15$ K; indexes in diagram refer to the equilibrium of eq 1. Experimental conditions: $I(NaNO_3) = 0.10$ mol·L^{-1}; $C_{UO2} = 4.0$ mmol·L^{-1}; $C_{paam} = 10$ mmol·L^{-1}.

Table 4. Formation Percentage of Species for UO_2−Low Molecular Weight Polyamine Systems at the Limit pH Value before Precipitation[a]

		% species formation			
UO_2−amine system	pH	112	111	110	11-1
UO_2−paam	5.5	0.5	6.2	57.7	35.6
UO_2−en	5.5			30.9	2.1
UO_2−ptr	6.0			27.0	28.9
UO_2−cdv	6.5			2.3	11.2
UO_2−spd	6.0		22.5	7.3	
UO_2−sper	6.0	8.2	29.1		

[a] Experimental conditions: $C_{UO2} = 4$ mmol·L^{-1}; $C_{amine} = 10$ mmol·L^{-1}; I ($NaNO_3$) = 0.1 mol·L^{-1}; $T = 298.15$ K.

Speciation Profiles of the Uranyl−Amine Systems. From the stability data obtained in the experimental conditions used in our investigation, it was possible to draw the species distribution as a function of pH. As an example we report in Figure 3 the distribution diagram of species formed in the UO_2−paam system in the pH range 3 to 6. By examining the diagram we can say that: (i) all of the species are present with high yields; (ii) no simple hydrolytic species of uranyl ion is present in the acidic pH range, and this demonstrates that the strong interaction between UO_2 and paam shifts the uranyl hydrolysis to higher pH values; and (iii) according to point (ii), a mixed hydrolytic species is formed at pH > 5, and it achieves more than 60 % formation at pH = 6. As pointed out before, the diagram was drawn at the reagent concentrations used in the experimental investigation. For these concentrations the formation of scarcely soluble oxo-species of uranium(VI) occurs at a pH higher than 6, and this makes it impossible to extend the diagram over this pH value.

Analogous considerations can be made also for the other UO_2−low molecular weight polyamine systems where precipitation of U(VI) oxo-species occurs in the pH range 5.5 to 6.5. At these pH values, quite consistent formation percentages of the 110 and 11-1 species are achieved in all of the systems investigated, as shown in Table 4. It is interesting to notice that, in spite of the decreasing stability of protonated species with respect to the unprotonated ones [see relationship (4)], a non-negligible formation percentage of the monoprotonated species (111) is also present at these pH values for the tri (spd)- and tetra (sper)-amine systems.

Quantitative Sequestering Capacity of Amines toward the Dioxouranium(VI) Cation. Amino groups play a very important role in coordination chemistry of several metal ions and

Table 5. Parameters of Equation 5a[a] for a Solution Containing $C_{UO_2} = 10^{-12}$ mol·L^{-1} (trace) in the Presence of Different Amines, at I(NaNO$_3$) = 0.1 mol·L^{-1}, at T = 298.15 K and at Different pH Values

	UO_2−en	UO_2−ptr	UO_2−cdv	UO_2−spd	UO_2−sper	UO_2−paam
pH	pL_{50}	pL_{50}	pL_{50}	pL_{50}	pL_{50}	pL_{50}
6	4.20	4.33	3.08	3.94	4.07	7.04
7	5.48	6.17	4.97	5.51	6.01	8.92
8	6.75	8.33	7.15	7.44	7.85	10.76

[a] S (slope in eqs 5 and 5a) = 0.434 for all pH values in all of the systems investigated.

contribute, as a single binding group or together with other binding groups, to modulate the metal accumulation in natural waters and in biological fluids. The control of metal accumulation generally occurs by binding the metal ions as a complex species with a consequent reduction of the free metal ion concentration and, therefore, of its bioavailability and toxicity. The higher the stability of the metal−ligand complex species formed, the more efficient is the process. A classical example refers to the sequestration of exceeding toxic metal ions in the human body by adding chelating agents with high metal-binding capacity. Owing to the wide diffusion of the biogenic amines in many biological fluids, it could be interesting to know what is the sequestering ability of these compounds, and, in general, of polyamines, toward uranyl ion. This ability is, of course, strictly related to the stability of the complex species formed by the interaction of the uranyl ion with amino group containing ligands.

The stability data obtained for the complex species formed in all of the systems investigated allowed us to quantitatively define the sequestration capacity of the polyamines toward UO_2^{2+}, by considering the amount of ligand necessary to bind the metal under fixed experimental conditions of pH, ionic medium, ionic strength, and temperature. To this end we used the following sigmoid-type Boltzmann equation[27]

$$P = P_\infty + \frac{P_0 - P_\infty}{1 + \exp[(pL - pL_{50})/S]} \tag{5}$$

where P is the total percentage of $M_pL_qH_r$ complex species (in this case M = UO_2^{2+}; L = amines) calculated with respect to metal concentration; $pL = -\log[L]_T$; P_0 and P_∞ are the percentages for $pL \to 0$ and $pL \to \infty$, respectively; $pL_{50} = pL$ (for P = 50 %); S is an adjustable parameter which accounts for the slope in the flex of the sigmoid curve. Since in our case $P_\infty = 0$ and $P_0 = 100$, eq 5 becomes:

$$\sum\% = \frac{100}{1 + \exp[(pL - pL_{50})/S]} \tag{5a}$$

where pL_{50} is the ligand concentration necessary to sequestrate 50 % of the uranyl ion. This equation allows the calculation of the UO_2 sequestration percentage at each pH and ligand concentration value, after the formation constants for the systems under investigation and the species formation percentages versus pH have been defined. In Table 5 we report the pL_{50} values, calculated by eq 5a, for the percentage sequestration of UO_2 (trace concentration) by the different amines in the pH range 6 to 8 of interest of many biological fluids and at 0.1 mol·L^{-1} ionic strength (NaNO$_3$ ionic medium). The pH range of investigation was extended over the pH limit of U(VI) oxide precipitation (pH ∼ 6) by assuming that (i) for a very low concentration of uranyl (10^{-12} mol·L^{-1}, trace concentration) no precipitation occurs, and (ii) the only species formed over pH = 6 is the mixed one [ML(OH), with M = UO_2^{2+}, L = amine]. Results reported in Table 5 show quite a regular increasing of pL_{50} with the pH increasing for all of the systems investigated. In particular, for the UO_2−paam system the pL_{50} increases about 2 log units per pH unit in the range 5 to 8.

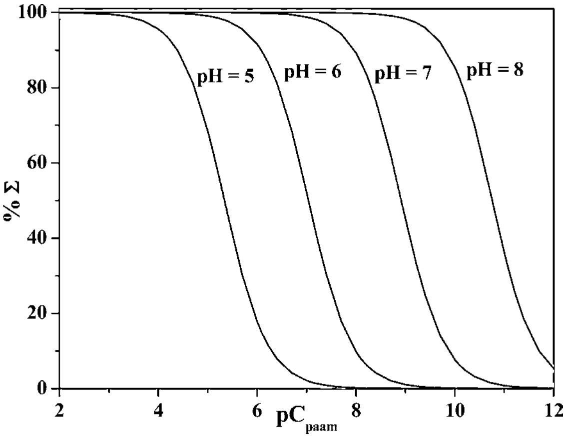

Figure 4. Sequestration percentage of uranyl by paam vs pC_{paam} at different pH values. Experimental conditions: I(NaNO$_3$) = 0.1 mol·L^{-1}; C_{UO2} = 10^{-12} mol·L^{-1}(trace); and T = 298.15 K.

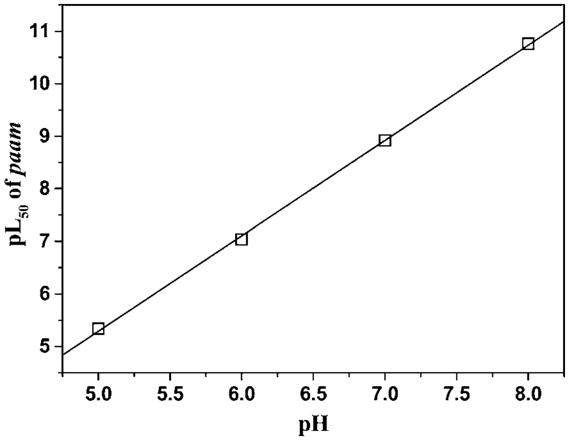

Figure 5. Dependence of pL_{50} values on the pH at I(NaNO$_3$) = 0.1 mol·L^{-1}, C_{UO2} = 10^{-12} mol·L^{-1}(trace); and T = 298.15 K.

Figure 4 shows the pL_{50} curves for paam at different pH values. As expected, because of the high stability of the complex species formed, paam shows a very good sequestering capacity toward the dioxouranium(VI) ion for all pH values considered. The best pH condition is at pH = 8 where only $10^{-10.76}$ mol·L^{-1} of paam is needed to sequestrate 50 % of UO_2^{2+} at 10^{-12} mol·L^{-1} concentration. The sequestering capacity of the polyamino-polyelectrolyte decreases dramatically for pH values lower than 6, that is, when amino groups are protonated: at pH = 5, about $10^{-5.3}$ mol·L^{-1} of paam is necessary to bind (to sequestrate) 50 % of UO_2^{2+} at the same concentration.

The dependence of pL_{50} on pH is linear, as shown in Figure 5, and can be expressed by the simple relationship:

$$pL_{50} = a(\text{pH} - 7 + b) \tag{6}$$

The empirical parameters a and b are reported in Table 6 for all of the systems studied in this work.

Comparison with Other Divalent Metal−Amine Complex Species. The absence in the literature of quantitative data on the formation of UO_2−amine complex species does not allow us to compare our results with those of other authors. On the contrary, the complexation capability of polyamines toward several divalent metal ions has been widely studied,[15−19] and,

Table 6. Empirical Parameters of Equation 6 for the Dependence of pL$_{50}$ on pH, at $I = 0.1$ mol·L^{-1}, in NaNO$_3$ Ionic Medium and at $T = 298.15$ K

amine	a	b	σ^a
en	1.28	5.47	< 0.01
ptr	2.00	6.30	0.08
cdv	2.03	5.08	0.07
spd	1.75	5.65	0.09
sper	1.89	5.97	0.03
paam	1.81	8.92	0.04

[a] Standard deviation on the fit.

Table 7. Formation Constants of the Complex Species M^{2+}−Ethylene Diamine at $I = 0.1$ mol·L^{-1} and $T = 298.15$ K

	log K^a					
species	Cu^{2+}	Cd^{2+}	Co^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
M(en)	10.49	5.40	5.5	7.30	5.05	5.69
M(en)$_2$	19.60	9.87	10.1	13.44	8.67	10.64
M(en)$_3$		12.1		17.51		13.02

[a] Ref 18.

in particular, among the diamines considered in this work, ethylenediamine has been most investigated. In Table 7 are reported the critically selected stability constants of metal complexes between ethylenediamine and some divalent metal ions.[18] By comparing the formation constants of the species ML (the only species present in all of the systems), we observe the stability scale:

$$\mathrm{Cu^{2+} > UO_2{}^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} \geq Cd^{2+} > Pb^{2+}}$$

The same stability trend was found in a previous work[30] regarding the sequestration capability of two dicarboxylic aminoacids, namely, aspartate and glutamate, toward the UO$_2^{2+}$ ion. Also in that case a comparison of the stability of 1:1 complex species formed by the two amino acids with some of the divalent metal ions here considered showed that only the copper(II) ion forms complexes stronger than those of UO$_2^{2+}$.

Final Remarks

In this paper we investigated the stability of complex species formed by some ligands, representative of the amine class, and the dioxouranium(VI) cation. In particular we must stress the following points.

Amines form quite strong complexes with the dioxouranium(VI) cation, as shown by the high stability constants (Table 3) and by the high pL$_{50}$ values.

The stability of these complexes is higher than that of carboxylic ligands. As an example, log K(UO$_2$−ethylene diamine) = 9.9, while log K(UO$_2$−malonate) = 5.7.[27] This trend is the same as that shown by several polycarboxylate ligands.[29] Of course, also for the sequestering capability, pL$_{50}$ (amines) > pL$_{50}$ (carboxylates).[29]

It is noticeable that high molecular weight polyamines behave in a similar way as low molecular weight amines.

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