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Enhancement of hydrolysis through the formation of mixed hetero-metal species

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Abstract

In order to analyze the formation of hetero-metal polynuclear hydrolytic species, in this paper, we reported some results of an investigation (at $I = 0.16\,\mathrm{mol\,L^{-1}}$ in $\mathrm{NaNO_3}$, at $t = 25\,^{\circ}\mathrm{C}$ by potentiometry, ISE-$\mathrm{H^+}$, glass electrode) on the hydrolysis of several mixtures (in different ratios) of two couples of cations: dioxouranium(VI)/copper(II) and dioxouranium(VI)/diethyltin(IV). The elevated total concentrations of cations $0.005 \le \Sigma C_\mathrm{M}\ \mathrm{mol\,L^{-1}} \le 0.05$) adopted in these measurements induced us to study again the hydrolysis of uranyl, for which no suitable literature data are available in these particular experimental conditions. All measurements were performed by two different operators, using completely independent instruments and reagents. Many different speciation models were considered in the calculations, including the simultaneous refinement of homo- and hetero-metal species, and a statistical analysis of obtained results was proposed too. Main results can be summarized as follows: $\mathrm{UO_2}^{2+}$ and Cu^{2+} form three hetero-metal polynuclear hydrolytic species [$\mathrm{(UO_2)Cu(OH)}^{3+}$, $\mathrm{(UO_2)Cu(OH)_2}^{2+}$ and $\mathrm{(UO_2)_2Cu(OH)_4}^{2+}$, with $\log \beta_\mathrm{pqr} = -2.93 \pm 0.01$, -7.34 ± 0.03 and -13.78 ± 0.03, respectively], all those common to their simple speciation without the other cation; $\mathrm{UO_2}^{2+}$ and $\mathrm{(C_2H_5)_2Sn}^{2+}$ form seven mixed hydrolytic species [$\mathrm{(UO_2)(DET)(OH)}^{3+}$, $\mathrm{(UO_2)(DET)(OH)_2}^{2+}$, $\mathrm{(UO_2)_2(DET)(OH)_4}^{2+}$, $\mathrm{(UO_2)(DET)_2(OH)_4}^{2+}$, $\mathrm{(UO_2)_2(DET)(OH)_5}^{+}$, $\mathrm{(UO_2)(DET)_2(OH)_5}^{+}$ and $\mathrm{(UO_2)_2(DET)(OH)_7}^{-}$, with $\log \beta_\mathrm{pqr} = -2.5 \pm 0.2$, -4.74 ± 0.02, -10.70 ± 0.06, -10.34 ± 0.03, -15.70 ± 0.06, -15.58 ± 0.06 and -27.9 ± 0.1, respectively] that are of the same kind of those formed by uranyl; formation of mixed hydrolytic species causes a significant enhancement of the percentage of hydrolyzed metal cations, modifying the solubility and, therefore, the bioavailability of these cations. We also determined, for dioxouranium(VI)/copper(II) system, the corresponding complex formation enthalpies and entropies by direct calorimetric measurements. We obtained $\Delta H_{112} = 47.9 \pm 0.6$ and $\Delta H_{214} = 92.9 \pm 0.5\,\mathrm{kJ\,mol^{-1}}$, $T\Delta S_{112} = 6 \pm 1$ and $T\Delta S_{214} = 14 \pm 1\,\mathrm{kJ\,mol^{-1}}$ (±S.D.), respectively, for the formation of $\mathrm{(UO_2)(Cu)(OH)_2}^{2+}$ and $\mathrm{(UO_2)_2(Cu)(OH)_4}^{2+}$ species (according to reaction 2). We also calculated the single enthalpic and entropic contributes to the extra-stability that these species show with respect to the corresponding homo polynuclear ones.

Keywords: Hydrolysis; Mixed species; Copper(II); Dioxouranium(VI); Diethyltin(IV)

1. Introduction

The environmental impact of heavy metals is a serious social problem, which interests scientists of many different research fields. Their behavior in natural waters is characterized by the formation of several complex species, with variable stability, owing to the presence of a wide number of inorganic and organic ligands. In almost all cases, these cations also undergo strong hydrolysis with the formation of many species [1]. It follows that, to fully appreciate how heavy metal cations behave in an aquatic environment, speciation studies (i.e. the study of the distribution of a component in the different species) are of fundamental importance. Moreover, it also very often happens that in natural

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or wastewaters they are present in mixtures of two or more cations with very variable concentration ranges and ratios. For this reason, together with the fact that the most of these cations forms many polynuclear hydrolytic species also at low concentrations, we thought it was of great importance to know if the formation of mixed “hetero-metal” hydrolytic species of two or more of these cations was possible and if the formation of these species was thermodynamically favored or not. In order to answer to these questions, we report in this paper a study (at $I = 0.16\,\text{mol L}^{-1}$ in $NaNO_3$, at $t = 25\,^{\circ}C$ by potentiometry, ISE-H^+, glass electrode) on the hydrolysis of several mixtures (in different ratios) of two couples of cations: dioxouranium(VI)/copper(II) and dioxouranium(VI)/diethyltin(IV). In order to provide a complete picture of the thermodynamic behavior of the mixed hydrolytic species, we also report, for the first system, corresponding complex formation enthalpies and entropies obtained by direct calorimetric measurements. We chose these two systems because of the importance that these three cations have in many research areas. Dioxouranium(VI) ($UO_2{}^{2+}$, also uranyl) is the main form in which uranium is present in nature, and its environmental hazard is due more to its high chemical toxicity towards a wide number living organisms than to its radioactivity [2,3]. Copper(II) (Cu^{2+}) is involved in many processes of environmental and biological relevance [4,5]. Diethyltin(IV) [$(C_2H_5)_2Sn^{2+}$, DET for short], is representative of the class of organotin(IV) compounds, the most industrially used organometallic compounds. Ethyl derivatives are also the most active groups towards mammals [6,7]. Moreover, the wide spectrum of applications of the three chosen cations has raised the number of anthropogenic input sources of these substances, in special case as regards natural waters. Essentially this aspect is the reason why studies on their chemical physical behavior and on their speciation in aqueous solutions are so abundant in literature, although the difficulties related to the determination of the stability of the complexes and, very often, to the nature of species formed too [8,9]. As, for example, concerns copper(II) hydrolysis, in one of the most exhaustive papers published on this topic [10], many references can be found. During the last decades research on uranium chemistry, and particularly on its hydrolysis [11–17], has expanded too. Also our research group has been dealing since some years with speciation studies of uranyl, copper(II), DET, with particular attention to their hydrolysis in several ionic media and ionic strengths, and to their binding ability towards a wide number of organic and inorganic ligands [6,18–24]. The three cations were coupled as the two systems investigated because of the similarities in the hydrolytic behavior of $UO_2{}^{2+}$ and Cu^{2+} (same kind of species formed) as regard first pair; on the contrary, the second opposite choice was made on the basis of the differences in the behavior of $UO_2{}^{2+}$ and $(C_2H_5)_2Sn^{2+}$, although of the strong tendency to hydrolysis that both cations show, starting from low pH values (less than pH = 3). In fact, exception done for $M_2(OH)_2{}^{2+}$ species, common for both uranyl and DET, no more hydrolytic species are similar for the two cations.

The high metal concentrations used in the measurements presented in this paper [in particular for $UO_2{}^{2+}/Cu^{2+}$ system and a part of $UO_2{}^{2+}/(C_2H_5)_2Sn^{2+}$] induced us to study again the hydrolysis of uranyl, for which no suitable data are available in these particular experimental conditions. As regards hydrolysis constants of Cu^{2+} and DET, we used already published values [6,20,23,24]. Owing to the complexity of the systems investigated, all measurements were performed by two different operators using completely independent instruments and reagents, and a statistical analysis of obtained results was proposed too.

2. Experimental section

2.1. Chemicals

Nitric acid and sodium hydroxide solutions were prepared by diluting concentrated ampoules (Riedel–deHaën), and were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. $NaNO_3$ was prepared by weighing pure salt (Fluka) dried in an oven at 110 °C. Dioxouranium(VI) and copper(II) were used in form of nitrate salts (Fluka), diethyltin(IV) in form of chloride salt (Alfa-Aesar). All cations were used without further purification and purity of dioxouranium(VI) was checked by gravimetric determination of uranium after ignition to the oxide U_3O_8. Purity of diethyltin(IV) was checked potentiometrically and copper(II) solutions were standardized spectrophotometrically. All purities resulted $\geq$99.5%. All solutions were prepared with analytical grade water ($R = 18\,\text{M}\Omega\,\text{cm}^{-1}$), using grade A glassware.

2.2. Apparatus and procedure

2.2.1. Potentiometric measurements

In order to minimize systematic errors, two operators carried out potentiometric titrations (at $t = 25.0 \pm 0.1\,^{\circ}C$) in a completely independent way, using completely different reagents and two separate systems: first one consisted of a Model 713 Metrohm potentiometer, equipped with an half cell glass electrode (Ross type 8101, from Orion), a double junction reference electrode (type 900200, from Orion) and a Model 765 Metrohm motorized burette; second one was a Crison micro-pH 2002 potentiometer, with the same kind of equipment of the first apparatus. Estimated accuracy was ±0.15 mV and ±0.003 mL for e.m.f. and titrant volume readings, respectively, and was the same for both systems. They were connected to a PC, and automatic titrations were performed using a suitable computer program to control titrant delivery, data acquisition and to check for e.m.f. stability. All titrations were carried out under magnetic stirring and bubbling through the solution purified presaturated N_2, in order to exclude O_2 and CO_2 inside. Potentiometric measurements were carried out by titrating 25 mL of the solution containing dif-

Table 1
Experimental conditions for measurements at $I = 0.16\,\mathrm{mol\,L^{-1}}$ and $t = 25\,^{\circ}\mathrm{C}$[a]

$(UO_2)(NO_3)_2$ ($\mathrm{mol\,L^{-1}}$)	$M(NO_3)_2$ ($\mathrm{mol\,L^{-1}}$)	$NaNO_3$ ($\mathrm{mol\,L^{-1}}$)	Titrations operator A[b]	Titrations operator B[b]
0.050	–	–	3	3
0.040	–	0.030	2	1
0.030	–	0.060	1	2
M = Cu^{2+}				
0.040	0.010	–	3	1
0.030	0.020	–	2	1
0.020	0.030	–	2	1
0.010	0.040	–	2	1
0.030	0.010	0.030	3	2
0.020	0.020	0.030	1	2
0.010	0.030	0.030	1	2
0.025	0.005	0.060	1	2
0.020	0.010	0.060	1	2
0.015	0.015	0.060	1	1
0.010	0.020	0.060	1	2
0.005	0.025	0.060	3	1
M = $(C_2H_5)_2Sn^{2+}$				
0.040	0.010	–	1	2
0.030	0.020	–	2	1
0.020	0.030	–	2	2
0.010	0.040	–	2	2
0.030	0.010	0.030	1	2
0.020	0.020	0.030	1	1
0.010	0.030	0.030	1	1
0.025	0.005	0.060	1	–
0.020	0.010	0.060	–	1
0.015	0.015	0.060	1	–
0.010	0.020	0.060	–	1
0.005	0.025	0.060	1	–
0.004	0.001	0.135	1	–
0.003	0.002	0.135	–	1
0.002	0.003	0.135	1	–
0.001	0.004	0.135	–	1

[a] $0.010\,\mathrm{mol\,L^{-1}}$ HNO_3 added in each titration.
[b] 80−100 exp. points for each titration.

ferent amounts of two metals (just UO_2^{2+} for its hydrolysis), nitric acid ($10\,\mathrm{mmol\,L^{-1}}$) and, eventually, the background salt ($NaNO_3$) in order to obtain pre-established ionic strength value ($I = 0.16\,\mathrm{mol\,L^{-1}}$), with standard NaOH solutions (at $I = 0.16$ and $0.20\,\mathrm{mol\,L^{-1}}$) until the formation of precipitate was noted (the pH of precipitation is dependent on the concentration and on the molar ratio of metals; for the UO_2^{2+}/Cu^{2+} system the measurements were performed in the pH range 2.1–5.0; whilst for the $UO_2^{2+}/(C_2H_5)_2Sn^{2+}$ system in the pH range 2.1–6.4). The choice of nitrate as counter ion was made because this anion is considered as weakly-interacting with the cations under study [25]. For each experiment, independent titrations of strong acid solution with standard base were carried out under the same medium and ionic strength conditions as the systems to be investigated, with the aim of determining electrode potential (E^0) and acidic junction potential ($E_j = j_a\,[H^+]$). 80–100 points for each titration were collected. All experimental conditions are reported in Table 1.

2.2.2. Calorimetric measurements

Calorimetric measurements were performed at 25.000 ± 0.001 °C by a Tronac isoperibolic titration calorimeter model 450 coupled with a Keithley 196 system Dmm digital multimeter. The measurements were performed at pH 5 by titrating 50 mL of solution containing UO_2^{2+} in variable amounts (5–$10\,\mathrm{mmol\,L^{-1}}$), $NaNO_3$ and NaOH in order to reach the pre-established values of ionic strength and pH. The titrant consisted of a solution of $Cu(NO_3)_2$ ($C_{Cu} \sim 0.3\,\mathrm{mol\,L^{-1}}$) and was added into the reaction cell till the total Cu^{2+}concentration was double respect to UO_2^{2+}. The titrant was delivered by a 2.5 mL capacity Hamilton syringe, model 1002TLL. For each experimental condition two measurements were performed. A computer program was used for the acquisition of the calorimetric data. The accuracy was checked by titrating a THAM [tris-(hydroxymethyl)amino-methane] buffer with HCl. The enthalpy of dilution was measured before each experiment under the same experimental conditions of the measurements. The accuracy of calorimetric apparatus was Q

± 0.008 J and the accuracy of the titrant volume was ±0.001 mL.

2.3. Calculations

The BSTAC [26] and STACO [27] computer programs were used in the refinement of all the parameters of an acid-base titration (E^0, pK_w, coefficient of junction potential j_a, analytical concentration of reagents) and in the calculation of hydrolysis constants. The ES4ECI [28] program was used to draw distribution diagrams and to calculate formation percentages of species. Calorimetric data were analyzed by the ES5CMI computer program [29].

Dioxouranium(VI), copper(II) and diethyltin(IV) hydrolysis constants, β_pq, are given according to the equilibrium

$$\mathrm{pM^{2+} + qH_2O = M_p(OH)_q{}^{(2p-q)} + qH^+} \quad \beta_\mathrm{pq} \tag{1}$$

mixed hydrolysis constants, β_prq, are given according to a similar equilibrium

$$\mathrm{pM^{2+} + rM'^{2+} + qH_2O = M_pM'_r(OH)_q{}^{(2p+2r-q)} + qH^+} \quad \beta_\mathrm{prq} \tag{2}$$

with $\mathrm{M^{2+} = UO_2{}^{2+}}$, and $\mathrm{M'^{2+} = Cu^{2+}}$ or $\mathrm{(C_2H_5)_2Sn^{2+}}$, for each group of measurements. All values are expressed in the molar (mol L^{-1}) concentration scale.

3. Results and discussion

3.1. Hydrolysis of dioxouranium(VI), copper(II), and diethyltin(IV)

Experimental conditions for the hydrolysis of $\mathrm{UO_2{}^{2+}}$ have already been reported in Table 1. According to previous work [18,19], we performed several trials to explain data in terms of uranyl hydrolytic species and, using literature information we took into account the following species (p,q): (1,1), (2,1), (1,2), (2,2), (3,4), (3,5), (3,7), (4,6), (4,7) (other species having higher p/q ratio were not considered since they are likely to be formed at pH >> 6, where precipitation of scarcely soluble species starts) [18,19]. After calculations, the formation of one mononuclear [$\mathrm{UO_2(OH)^+}$], two binuclear [$\mathrm{(UO_2)_2(OH)^{3+}}$ and $\mathrm{(UO_2)_2(OH)_2{}^{2+}}$] and three trinuclear [$\mathrm{(UO_2)_3(OH)_4{}^{2+}}$, $\mathrm{(UO_2)_3(OH)_5{}^+}$ and $\mathrm{(UO_2)_3(OH)_7{}^-}$] species seemed to be the best speciation model, in great agreement with literature data [18,19,30]. The presence of the further $\mathrm{(UO_2)_2(OH)^{3+}}$ species is not inconsistent with previous results, due to the higher metal concentrations used in the present study respect to refs. [18,19] ($10 \le C_\mathrm{UO_2}$ mmol L^{-1} ≤ 50 this work, $0.5 \le C_\mathrm{UO_2}$ mmol L^{-1} ≤ 5 refs. [18,19]). Results are shown in Table 2, where hydrolysis constants for dioxouranium(VI) obtained in this work are reported together with those of copper(II) and diethyltin(IV) [6,20,23,24]. The importance of the hydrolytic species of uranyl is illustrated in Fig. 1, which shows the formation percentage of these species as function of pH. As can be seen, hydrolysis of uranyl starts at low pH values and become already significant before pH ~3, when the cation is hydrolyzed for more than 30%. In the same speciation diagram can be also noted how, in the proposed experimental conditions, the mononuclear species is not present, as $\mathrm{(UO_2)_3(OH)_7{}^-}$, whilst $\mathrm{(UO_2)_2(OH)^{3+}}$ shows low formation percentages. Main species result to be polynuclear ones, with formation percentages that reach ~80%, in the case of $\mathrm{(UO_2)_3(OH)_5{}^+}$. However, $\mathrm{UO_2(OH)^+}$, $\mathrm{(UO_2)_2(OH)^{3+}}$ and $\mathrm{(UO_2)_3(OH)_7{}^-}$ are formed in significant amounts in other experimental conditions utilized in the paper, and must be considered for a more correct speciation model.

Table 2
Overall hydrolysis constants of $\mathrm{UO_2{}^{2+}}$, $\mathrm{Cu^{2+}}$ and $\mathrm{(C_2H_5)_2Sn^{2+}}$ species at I = 0.16 mol L^{-1} and t = 25 °C

Reaction	log β_pq[a]
$\mathrm{UO_2{}^{2+} + H_2O = UO_2OH^+ + H^+}$	−5.79 ± 0.12
$\mathrm{2UO_2{}^{2+} + H_2O = (UO_2)_2OH^{3+} + 2H^+}$	−3.83 ± 0.05
$\mathrm{2UO_2{}^{2+} + 2H_2O = (UO_2)_2(OH)_2{}^{2+} + 2H^+}$	−5.932 ± 0.002
$\mathrm{3UO_2{}^{2+} + 4H_2O = (UO_2)_3(OH)_4{}^{2+} + 4H^+}$	−12.79 ± 0.01
$\mathrm{3UO_2{}^{2+} + 5H_2O = (UO_2)_3(OH)_5{}^+ + 5H^+}$	−16.457 ± 0.007
$\mathrm{3UO_2{}^{2+} + 7H_2O = (UO_2)_3(OH)_7{}^- + 7H^+}$	−28.58 ± 0.05
$\mathrm{Cu^{2+} + H_2O = CuOH^+ + H^+}$	−7.70[b]
$\mathrm{2Cu^{2+} + H_2O = (Cu)_2OH^{3+} + 2H^+}$	−6.08
$\mathrm{2Cu^{2+} + 2H_2O = (Cu)_2(OH)_2{}^{2+} + 2H^+}$	−10.89
$\mathrm{3Cu^{2+} + 4H_2O = (Cu)_3(OH)_4{}^{2+} + 4H^+}$	−19.97
$\mathrm{DET + H_2O = (DET)(OH)^+ + H^+}$	−3.20[c]
$\mathrm{DET + 2H_2O = (DET)(OH)_2{}^0 + 2H^+}$	−8.66
$\mathrm{DET + 3H_2O = (DET)(OH)_3{}^- + 3H^+}$	−20.02
$\mathrm{2DET + 2H_2O = (DET)_2(OH)_2{}^{2+} + 2H^+}$	−4.97
$\mathrm{2DET + 3H_2O = (DET)_2(OH)_3{}^+ + 3H^+}$	−10.19

[a] ±3 S.D.
[b] Refs. [20,23,24].
[c] Ref. [6].

3.2. Hydrolysis of dioxouranium(VI)/copper(II) system

From the analysis of experimental data by both STACO and BSTAC computer programs, the sets of operators A and

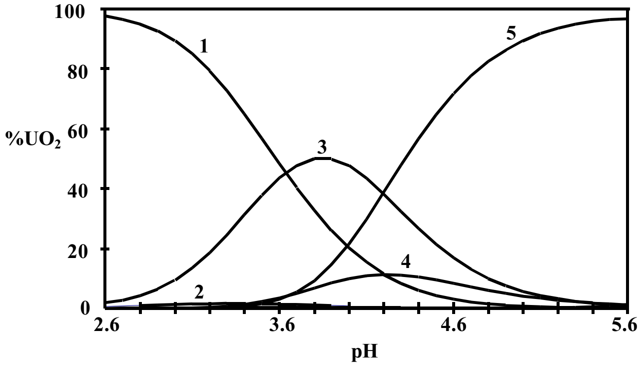

Fig. 1. Distribution diagram of dioxouranium(VI) species vs. pH at t = 25 °C. Species: 1, $\mathrm{UO_2}$; 2, $\mathrm{(UO_2)_2(OH)}$; 3, $\mathrm{(UO_2)_2(OH)_2}$; 4, $\mathrm{(UO_2)_3(OH)_4}$; 5, $\mathrm{(UO_2)_3(OH)_5}$; (charges omitted for simplicity). Simulation conditions: $C_\mathrm{UO_2}$ = 0.05 mol L^{-1}; I = 0.16 mol L^{-1}.

B furnished the same kind of results. The accepted model was the one that includes the formation of three hetero-metal hydrolytic species, $(UO_2)Cu(OH)^{3+}$, $(UO_2)Cu(OH)_2{}^{2+}$ and $(UO_2)_2Cu(OH)_4{}^{2+}$. The values of the constants, according to Eq. (2), are shown in Table 3. This speciation model was preferred to another one including $(UO_2)_2Cu(OH)_5{}^{+}$ species instead of $(UO_2)_2Cu(OH)_4{}^{2+}$. Several trials were performed in order to select the best model, and only an accurate statistical analysis on the results obtained from the two separate sets, and from the total set, removed all doubts. Some of these results for main tested models, together with the value of corresponding ratios between single variances and that one of accepted model are reported in Table 4. Owing to the very high number of degree of freedom of the system, due to the wide number of experimental points acquired, also the very low values of ratios shown in Table 4 resulted to be significant at a 95% confidence interval. The ultimate criteria used to select the chemical model are: (a) the agreement between results of the dataset of operators A and B; (b) the value of the variance ratio; (c) the simplicity of the model (other minor species can be added to the chosen ones but the model become unrealistically complicated); (d) the likelihood of the proposed species, in particular in relation to homopolynuclear species. As a further check, during calculations, we also refined some of these last species together with mixed ones, without sensibly alter the values of hydrolysis constants for each species. For example, in one of these calculations we obtained (±3 S.D.): $\log \beta_{111} = -3.02 \pm 0.03$; $\log \beta_{112} = -7.39 \pm 0.03$; $\log \beta_{214} = -13.69 \pm 0.03$ and, for

Table 3
Overall hetero-metal hydrolysis constants of $UO_2{}^{2+}/Cu^{2+}$ system at I = 0.16 mol L^{-1} and t = 25 °C

Reaction	$\log \beta_{pqr}$[a]
$UO_2{}^{2+} + Cu^{2+} + H_2O = (UO_2)Cu(OH)^{3+} + H^+$	-2.93 ± 0.01
$UO_2{}^{2+} + Cu^{2+} + 2H_2O = (UO_2)Cu(OH)_2{}^{2+} + 2H^+$	-7.34 ± 0.03
$2UO_2{}^{2+} + Cu^{2+} + 4H_2O = (UO_2)_2Cu(OH)_4{}^{2+} + 4H^+$	-13.78 ± 0.03

[a] ±3 S.D.

Table 4
Overall hetero-metal hydrolysis constants of $UO_2{}^{2+}/Cu^{2+}$ system for some proposed speciation models and comparisons with the accepted one (total data set)

$MM'(OH)^{3+}$[a]	$MM'(OH)_2{}^{2+}$[a]	$M_2M'(OH)_4{}^{2+}$[a]	$M_2M'(OH)_5{}^{+}$[a]	σ^2/σ_0^2
Total dataset				
-2.925 ± 0.006[b]	-7.342 ± 0.009[b]	-13.78 ± 0.01[b]		1.000[c]
-3.043 ± 0.006	-7.144 ± 0.003		-20.5 ± 0.3[b]	1.028
-3.23 ± 0.01				2.241
	-7.167 ± 0.004			1.226
		-13.546 ± 0.004		1.564
			-18.85 ± 0.01	2.030
-3.043 ± 0.007	-7.143 ± 0.003			1.028
-2.807 ± 0.004		-13.354 ± 0.002		1.050
-2.880 ± 0.005	1.701		-18.443 ± 0.009	
Operator A				
-2.82 ± 0.01[b]	-7.25 ± 0.02[b]	-13.88 ± 0.03[b]		1.000[d]
-2.89 ± 0.01	-7.107 ± 0.009		-20.2 ± 0.1[b]	1.015
-3.22 ± 0.04				2.336
	-7.152 ± 0.004			1.296
		-13.61 ± 0.01		1.668
			-18.98 ± 0.02	2.059
-2.90 ± 0.01	-7.093 ± 0.007			1.014
-2.683 ± 0.009		-13.337 ± 0.007		1.082
-2.80 ± 0.01	1.745		-18.53 ± 0.02	
Operator B				
-2.957 ± 0.007[b]	-7.62 ± 0.03[b]	-13.55 ± 0.02[b]		1.000[e]
-3.19 ± 0.01				2.273
	-7.180 ± 0.003			1.223
		-13.475 ± 0.003		1.522
			-18.62 ± 0.02[b]	2.089
-3.136 ± 0.008	-7.178 ± 0.004			1.058
-2.885 ± 0.005		-13.343 ± 0.005		1.019
-2.912 ± 0.003			-18.28 ± 0.01	1.689

[a] $M = UO_2{}^{2+}$, $M' = Cu^{2+}$.
[b] ±S.D.
[c] $\sigma_0 = 1.366$.
[d] $\sigma_0 = 1.464$.
[e] $\sigma_0 = 1.273$.

$(UO_2)_2(OH)_2{}^{2+}$ species, log $\beta_{202} = -5.90 \pm 0.01$, against values reported in Tables 2 and 3. The homogeneity of values demonstrate that the formation of mixed species during calculations by computer programs is not a fictitious improvement in fittings coming out from a simple minimization of experimental errors. Moreover, the three chosen species are of the same kind of those formed by both copper(II) and dioxouranium(VI) cations (M_2OH^{3+}, $M_2(OH)_2{}^{2+}$ and $M_3(OH)_4{}^{2+}$) [18–20,23,24]. This last aspect allowed us to calculate the "extra-stability" for the formation of the mixed hydrolytic species respect to the homo-polynuclear ones. In fact, the stability of mixed species can be examined by statistical analysis, considering the formation of this species starting from the simple hydrolytic complexes with just one metal cation [31]. The statistical value for the constant X related to the equilibrium between hydrolytic species of the same kind

$$\mathrm{i\,M_pA + j\,M'_rA = h\,M_iM'_jA} \quad X_{\mathrm{exp}} \tag{3}$$

with A = $(OH)_q$ for our case, is given by

$$X_{\mathrm{stat}} = [\mathrm{h!/i!j!}]^{\mathrm{h}} \quad X_{\mathrm{stat}} \tag{4}$$

It means that, as regards the formation of our proposed mixed hydrolytic species, X_{stat} are 4, 4 and 27 for M_2OH^{3+}, $M_2(OH)_2{}^{2+}$ and $M_3(OH)_4{}^{2+}$, respectively (i.e. log X_{stat} = 0.60, 0.60, 1.43). On the basis of the values of hydrolysis constants of the "hetero-metal" species and of those of the "homo-metal" ones, the log X_{exp} are

$$\log X_{111} = 2\log\beta_{111} - \log\beta_{201} - \log\beta_{021} = 4.05 \tag{5}$$

$$\log X_{112} = 2\log\beta_{112} - \log\beta_{202} - \log\beta_{022} = 2.14 \tag{6}$$

$$\log X_{214} = 3\log\beta_{214} - 2\log\beta_{304} - \log\beta_{034} = 4.21 \tag{7}$$

These values are a numerical index of the above-hypothesized "extra stability", a clear evidence of the fact that the formation of mixed hydrolytic species is thermodynamically favored. A direct consequence is the significant formation percentage that the hetero-metal species reach in these systems, as illustrated, for example, in the speciation diagram of Fig. 2, related to the distribution of the uranyl species in one of the dioxouranium(VI)/copper(II) investigated mixtures: e.g., in this case, $(UO_2)_2Cu(OH)_4{}^{2+}$ formation percentage reach 40%. In terms of hydrolysis, the formation of these mixed species causes in the $UO_2{}^{2+}/Cu^{2+}$ system a significant enhancement of the percentage of hydrolyzed metal cations (∼10% in Fig. 3), and this demonstrates again that hetero-polynuclear hydrolytic species cannot be neglected in a correct speciation model.

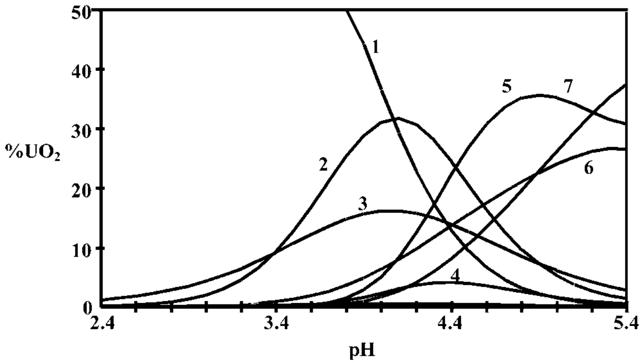

Fig. 2. Distribution diagram of dioxouranium(VI) species vs. pH at t = 25 °C in a $UO_2{}^{2+}/Cu^{2+}$ system. Species: 1, UO_2; 2, $(UO_2)_2(OH)_2$; 3, $(UO_2)Cu(OH)$; 4, $(UO_2)_3(OH)_4$; 5, $(UO_2)_3(OH)_5$; 6, $(UO_2)Cu(OH)_2$; 7, $(UO_2)_2Cu(OH)_4$ (charges omitted for simplicity). Simulation conditions: C_{UO_2} = 0.01 mol L^{-1}; C_{Cu} = 0.04 mol L^{-1}, I = 0.16 mol L^{-1}.

A more detailed and extensive discussion on the statistical prediction of the strength of complex formation constants for mixed species was given by Beck and Nagypal [31]. In addition to the previous treatment, we also adopted the same kind of statistical interpretation of these authors for the formation of mixed heterometal polynuclear hydrolytic species. As an example, we applied this method to calculate the statistical value for the formation of $MM'(OH)^{3+}$ species. Using this alternative approach, the statistical value X_{stat}, is given by [31]

$$X_{\mathrm{stat}} = 2 + (\beta_{101}/\beta_{011})\,(K_{021}/K_{201})^{1/2} + (\beta_{011}/\beta_{101})\,(K_{201}/K_{021})^{1/2} \tag{8}$$

where K_{pqr} refer to reaction (valid also for M′, exchanging M by M′ and p by r)

$$\mathrm{M_{(p-1)}(OH)_q^{(2p-q-1)} + M^{2+} = M_p(OH)_q^{(2p-q)}} \quad K_{\mathrm{pqr}} \tag{9}$$

and $K_{pqr} = \beta_{pqr}/\beta_{(p-1)qr}$. The value of log X_{stat} for the formation of $MM'(OH)^{3+}$ species, calculated in this way, resulted to be log X_{stat}=1.76. As can be seen, although this value is higher than the corresponding one calculated by the "simple statistical approach", it is in any case considerably lower than the log X_{111} value obtained. This means that the assumptions previously made (i.e., the formation of mixed hydrolytic species is thermodynamically favored) are correct.

In order to provide a complete picture of the thermodynamic behavior of the mixed hydrolytic species, we also determined corresponding complex formation enthalpies and

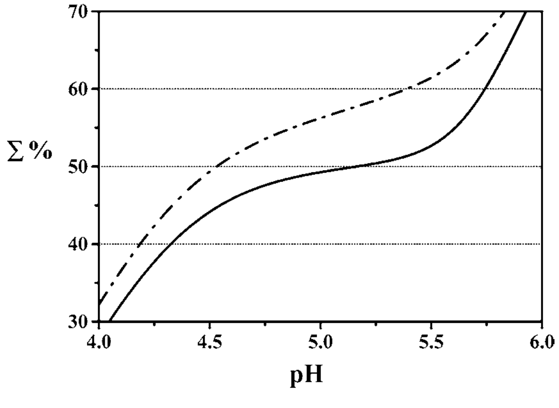

Fig. 3. Hydrolysis in $UO_2{}^{2+}/Cu^{2+}$ system. Percentage of hydrolyzed metal cations vs. pH. Simulation conditions: C_{UO_2} = 0.01 mol L^{-1}; C_{Cu} = 0.01 mol L^{-1}, I = 0.16 mol L^{-1}. Straight line: mixed species not considered; dash-dot line: mixed species considered.

entropies by direct calorimetric measurements. The formation enthalpies of the hydrolytic species of dioxouranium at I = 0.16 mol L^{-1} were calculated by interpolating values at different ionic strengths [32] (ΔH_{101} = 40.3 kJ mol^{-1}; ΔH_{202} = 46.2 kJ mol^{-1}; ΔH_{304} = 95.8 kJ mol^{-1}; ΔH_{305} = 115.7 kJ mol^{-1}; ΔH_{307} = 171.4 kJ mol^{-1}; the species $(UO_2)_2OH^{3+}$ was neglected in the calorimetric measurements because its low formation percentage in these experimental conditions). The formation enthalpies of hydrolytic species of copper(II) were taken from ref. 24 (ΔH_{011} = 8.5 kJ mol^{-1}; ΔH_{021} = 46.1 kJ mol^{-1}; ΔH_{022} = 18.4 kJ mol^{-1}; ΔH_{034} = 26.0 kJ mol^{-1}). In the experimental conditions adopted for this kind of measurements, already reported in a previous section, we did not obtain results for the $(UO_2)(Cu)(OH)^{3+}$ species, owing to the fact that this species is not formed in appreciable amounts at this particular pH value (pH ~5; e.g. see also Fig. 2). As concerns other species, we obtained: $\Delta H_{112} = 47.9 \pm 0.6$ and $\Delta H_{214} = 92.9 \pm 0.5$ kJ mol^{-1}, $T\Delta S_{112} = 6 \pm 1$ and $T\Delta S_{214} = 14 \pm 1$ kJ mol^{-1} (±S.D.), respectively, for the formation of $(UO_2)(Cu)(OH)_2{}^{2+}$ and $(UO_2)_2(Cu)(OH)_4{}^{2+}$ species (according to reaction 2). Moreover, we also determined the enthalpic and entropic contribute to the "extra stability" of these species, calculating the formation of these species starting from homo-polynuclear ones, as we did for the hydrolysis constants (when we determined the log X_{pqr}). During the calculations of these contributes, namely $\Delta H_{X_{pqr}}$ and $T\Delta S_{X_{pqr}}$, we utilized our previous values for formation enthalpies and entropies of dioxouranium [32] and copper [24] hydrolytic species. Calculated $\Delta H_{X_{pqr}}$ and $T\Delta S_{X_{pqr}}$ for $(UO_2)(Cu)(OH)_2{}^{2+}$ and $(UO_2)_2(Cu)(OH)_4{}^{2+}$ species are as follows

$$\Delta H_{X_{112}} = 2\,\Delta H_{112} - \Delta H_{202} - \Delta H_{022} = -27.4 \qquad (10)$$

$$\Delta H_{X_{214}} = 3\,\Delta H_{214} - 2\Delta H_{304} - \Delta H_{034} = -21.7 \qquad (11)$$

$$T\Delta S_{X_{112}} = 2\,T\Delta S_{112} - T\Delta S_{202} - T\Delta S_{022} = -15 \qquad (12)$$

$$T\Delta S_{X_{214}} = 3\,T\Delta S_{214} - 2T\Delta S_{304} - T\Delta S_{034} = 1 \qquad (13)$$

These results indicate that the main contribution to the extra-stability is enthalpic in nature.

3.3. *Hydrolysis of dioxouranium(VI)–diethyltin(IV) system*

Experimental conditions concerning the study of the formation of hetero-metal hydrolytic species of $UO_2{}^{2+}$ and $(C_2H_5)_2Sn^{2+}$ were already reported in Table 1. As for $UO_2{}^{2+}/Cu^{2+}$ system, STACO and BSTAC computer programs furnished similar results for the data sets of operators A and B. Also for this system, several models were proposed and, again, a statistical evaluation of obtained results was made, in order to be sure about the choice of rejecting the hypothesis of different models. As above mentioned, although the strong tendency to hydrolysis of both cations, the analysis of the informations obtained by the proposed and accepted model revealed a slight predominance of uranyl hydrolysis respect to DET, because of the formation of mixed species that are of the typical kind of those formed by dioxouranium(VI). In fact, of the seven species found, only $(UO_2)(DET)(OH)_2{}^{2+}$ is of the type common to diethyltin(VI) too $[M_2(OH)_2{}^{2+}]$. The remaining six are: $(UO_2)(DET)(OH)^{3+}$, $(UO_2)_2(DET)(OH)_4{}^{2+}$, $(UO_2)(DET)_2(OH)_4{}^{2+}$, $(UO_2)_2(DET)(OH)_5{}^{+}$, $(UO_2)(DET)_2(OH)_5{}^{+}$ and $(UO_2)_2(DET)(OH)_7{}^{-}$ [6,18,19]. The values of the constants, according to Eq. (2), are shown in Table 5. Furthermore, main results related to some of the several tested models, together with the accepted one, are reported in Table 6 for data sets of operators A and B, and for total set. As already mentioned for the uranyl–copper(II) system, the wide number of measurements allowed us to consider as "significant" the differences between variance of accepted model and the others. Also for this system, during calculations, we refined some of simple species together with mixed ones, without sensibly alter the values of hydrolysis constants for each species. For example, in one of these calculations we obtained (±3S.D.): log $\beta_{112} = -2.2 \pm 0.2$; log $\beta_{112} = -4.68 \pm 0.03$; log $\beta_{214} = -10.62 \pm 0.03$; log $\beta_{124} = -10.35 \pm 0.03$; log $\beta_{215} = -15.56 \pm 0.06$; log $\beta_{125} = -15.58 \pm 0.06$; log $\beta_{217} = -27.8 \pm 0.1$ and, for $(DET)_2(OH)_2{}^{2+}$ species, log $\beta_{022} = -5.09 \pm 0.03$, against values reported in Tables 2 and 5. The calculation of log X_{exp} for $(UO_2)(DET)(OH)_2{}^{2+}$, the only possible case, gave

$$\log X_{112} = 2\log\beta_{112} - \log\beta_{202} - \log\beta_{022} = 1.42 \qquad (14)$$

against the statistical value log X_{stat} = 0.60. Another interesting aspect of dioxouranium(VI)/diethyltin(IV) system emerges from the analysis of Figs. 4 and 5 where two speciation diagrams for uranyl in this system are reported, realized in two different experimental conditions, i.e. the same $UO_2{}^{2+}/(C_2H_5)_2Sn^{2+}$ ratio, but two varied total concentrations. In fact, in second diagram, where total concentration of ions is ten times higher, not only dioxouranium(VI) speciation is simpler than in the first one, but the importance of the species is different too. As can be seen, at high metal concentrations (Fig. 5), speciation is completely dominated by mixed hydrolytic species, whilst, with lower amounts of metals, simple homo-metal species are present too (Fig. 4). Although the two diagrams are calculated considering the same $UO_2{}^{2+}/(C_2H_5)_2Sn^{2+}$

Table 5
Overall hetero-metal hydrolysis constants of $UO_2{}^{2+}/(C_2H_5)_2Sn^{2+}$ system at I = 0.16 mol L^{-1} and t = 25 °C [$(C_2H_5)_2Sn^{2+}$=DET]

Reaction	log β_{pqr}[a]
$UO_2{}^{2+} + DET + H_2O = (UO_2)(DET)(OH)^{3+} + H^+$	-2.5 ± 0.2
$UO_2{}^{2+} + DET + 2H_2O = (UO_2)(DET)(OH)_2{}^{2+} + 2H^+$	-4.74 ± 0.02
$2UO_2{}^{2+} + DET + 4H_2O = (UO_2)_2(DET)(OH)_4{}^{2+} + 4H^+$	-10.70 ± 0.06
$UO_2{}^{2+} + 2DET + 4H_2O = (UO_2)(DET)_2(OH)_4{}^{2+} + 4H^+$	-10.34 ± 0.03
$2UO_2{}^{2+} + DET + 5H_2O = (UO_2)_2(DET)(OH)_5{}^{+} + 5H^+$	-15.70 ± 0.06
$UO_2{}^{2+} + 2DET + 5H_2O = (UO_2)(DET)_2(OH)_5{}^{+} + 5H^+$	-15.58 ± 0.06
$2UO_2{}^{2+} + DET + 7H_2O = (UO_2)_2(DET)(OH)_7{}^{-} + 7H^+$	-27.9 ± 0.1

[a] ±3 S.D.

Table 6
Overall hetero-metal hydrolysis constants of $UO_2^{2+}/(C_2H_5)_2Sn^{2+}$ system for some proposed speciation models and comparisons with the accepted one (total data set)

$MM'(OH)^{3+}$[a]	$MM'(OH)_2^{2+}$[a]	$M_2M'(OH)_4^{2+}$[a]	$MM'_2(OH)_4^{2+}$[a]	$M_2M'(OH)_5^{+}$[a]	$MM'_2(OH)_5^{+}$[a]	$M_2M'(OH)_7^{-}$[a]	σ^2/σ_0^2
Total dataset							
−2.45 ± 0.05[b]	−4.735 ± 0.005[b]	−10.70 ± 0.02[b]	−10.34 ± 0.01[b]	−15.70 ± 0.02[b]	−15.58 ± 0.02[b]	−27.93 ± 0.04[b]	1.000[c]
	−4.776 ± 0.002	−10.787 ± 0.005	−10.426 ± 0.006	−15.85 ± 0.01	−15.67 ± 0.02	−28.21 ± 0.05	1.006
	−4.781 ± 0.002	−10.795 ± 0.005	−10.429 ± 0.007	−15.88 ± 0.01	−15.64 ± 0.01		1.014
−2.64 ± 0.07	−4.754 ± 0.005	−10.77 ± 0.01	−10.33 ± 0.01	−15.61 ± 0.01		−27.67 ± 0.04	1.054
	−4.785 ± 0.002	−10.834 ± 0.006	−10.375 ± 0.006	−15.705 ± 0.008		−27.83 ± 0.04	1.099
Operator A							
−2.40 ± 0.06[b]	−4.755 ± 0.006[b]	−10.74 ± 0.01[b]	−10.26 ± 0.01[b]	−15.80 ± 0.03[b]	−15.49 ± 0.03[b]	−27.87 ± 0.06[b]	1.000[d]
	−4.798 ± 0.003	−10.847 ± 0.007	−10.351 ± 0.007	−16.01 ± 0.03	−15.56 ± 0.03	−28.22 ± 0.06	1.007
	−4.806 ± 0.002	−10.860 ± 0.007	−10.347 ± 0.007	−16.00 ± 0.02	−15.64 ± 0.03		1.019
−2.8 ± 0.1	−4.782 ± 0.007	−10.85 ± 0.02	−10.27 ± 0.01	−15.68 ± 0.02		−27.94 ± 0.06	1.113
	−4.799 ± 0.003	−10.892 ± 0.007	−10.312 ± 0.005	−15.74 ± 0.01		−28.11 ± 0.06	1.117
Operator B							
−2.49 ± 0.07[b]	−4.727 ± 0.007[b]	−10.62 ± 0.01[b]	−10.53 ± 0.02[b]	−15.58 ± 0.02[b]	−15.74 ± 0.04[b]	−27.91 ± 0.06[b]	1.000[e]
	−4.763 ± 0.002	−10.696 ± 0.009	−10.61 ± 0.02	−15.67 ± 0.01	−15.88 ± 0.05	−28.09 ± 0.06	1.007
	−4.764 ± 0.002	−10.690 ± 0.009	−10.64 ± 0.02	−15.72 ± 0.02	−15.73 ± 0.03		1.013
−2.7 ± 0.1	−4.746 ± 0.006	−10.67 ± 0.01	−10.51 ± 0.02	−15.54 ± 0.02		−27.65 ± 0.05	1.039
	−4.764 ± 0.003	−10.715 ± 0.009	−10.56 ± 0.01	−15.59 ± 0.01		−27.75 ± 0.04	1.045

[a] $M = UO_2^{2+}$, $M' = (C_2H_5)_2Sn^{2+}$.
[b] ±S.D.
[c] $\sigma_0 = 0.952$.
[d] $\sigma_0 = 0.917$.
[e] $\sigma_0 = 0.983$.

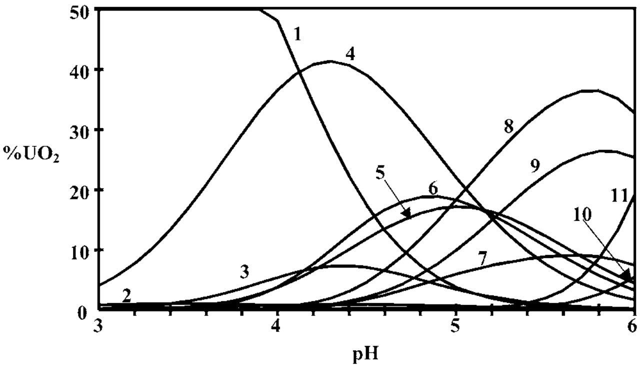

Fig. 4. Distribution diagram of dioxouranium(VI) species vs. pH at $t = 25\,°C$ in a $UO_2^{2+}/(C_2H_5)_2Sn^{2+}$ system. Species: 1, UO_2; 2, $(UO_2)(DET)(OH)$; 3, $(UO_2)_2(OH)_2$; 4, $(UO_2)(DET)(OH)_2$; 5, $(UO_2)(DET)_2(OH)_4$; 6, $(UO_2)_2(DET)(OH)_4$; 7, $(UO_2)_3(OH)_5$; 8, $(UO_2)_2(DET)(OH)_5$; 9, $(UO_2)(DET)_2(OH)_5$; 10, $(UO_2)_3(OH)_7$; 11, $(UO_2)_2(DET)(OH)_7$ (charges omitted for simplicity). Simulation conditions: $C_{UO_2} = 0.001\,mol\,L^{-1}$; $C_{DET} = 0.004\,mol\,L^{-1}$, $I = 0.16\,mol\,L^{-1}$.

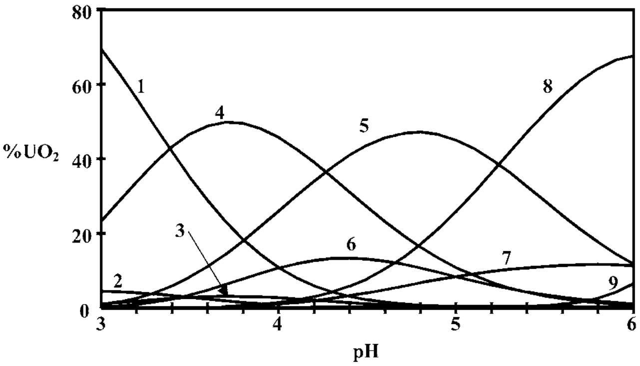

Fig. 5. Distribution diagram of dioxouranium(VI) species *vs*. pH at $t = 25\,°C$ in a $UO_2^{2+}/(C_2H_5)_2Sn^{2+}$ system. Species: 1, UO_2; 2, $(UO_2)(DET)(OH)$; 3, $(UO_2)_2(OH)_2$; 4, $(UO_2)(DET)(OH)_2$; 5, $(UO_2)(DET)_2(OH)_4$; 6, $(UO_2)_2(DET)(OH)_4$; 7, $(UO_2)_2(DET)(OH)_5$; 8, $(UO_2)(DET)_2(OH)_5$; 9, $(UO_2)_2(DET)(OH)_7$ (charges omitted for simplicity). Simulation conditions: $C_{UO_2} = 0.01\,mol\,L^{-1}$; $C_{DET} = 0.04\,mol\,L^{-1}$, $I = 0.16\,mol\,L^{-1}$.

ratio, ratios between hydrolytic species of the same kind are different. A clear example are tri-nuclear hetero-metal species: in Fig. 5, those with two DET and one uranyl cation are preferred respect to the corresponding species with two dioxouranium(VI) and one organotin(IV) cation; in Fig. 4, an opposite behavior is observed, i.e. species with two dioxouranium(VI) and one diethyltin(IV) cations reach an higher formation percentage. As observed for UO_2^{2+}/Cu^{2+}, also in the present system the formation of the mixed species causes a similar enhancement of the percentage of hydrolyzed metal cations (∼10% in Fig. 6), demonstrating again that hetero-polynuclear hydrolytic species cannot be neglected in a correct speciation model, also for $UO_2^{2+}/(C_2H_5)_2Sn^{2+}$ mixtures.

3.4. Comparisons with literature

In spite of the wide number of literature present on the hydrolysis of metal cations in various ionic media and ionic strengths, not many papers were published on the formation of mixed hetero-metal hydrolytic species. Just few research groups are involved in this kind of investigations.

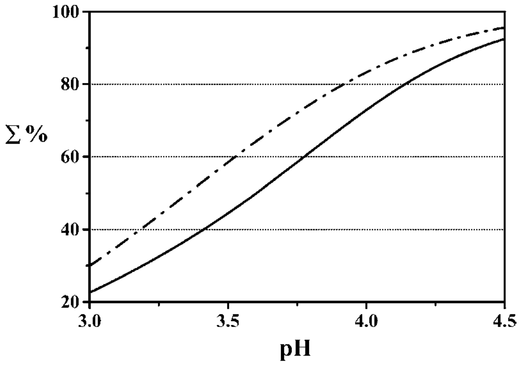

Fig. 6. Hydrolysis in $UO_2^{2+}/(C_2H_5)_2Sn^{2+}$ system. Percentage of hydrolyzed metal cations vs. pH. Simulation conditions: $C_{UO_2} = 0.01\ mol\ L^{-1}$; $C_{DET} = 0.01\ mol\ L^{-1}$, $I = 0.16\ mol\ L^{-1}$. Straight line: mixed species not considered; dash-dot line: mixed species considered.

In particular, from our researches, resulted that the most of studies were conducted by Russian and Belorussian scientists, using different techniques on several binary systems. Mixed hydrolysis of uranyl was analyzed just with aluminum, whilst copper(II) was utilized for the investigation of binary systems with Cr(III), Co(II), Al(III), Sc(III), Fe(III), Ni(II) [33–42]. No data were found on mixed hydrolysis of diethyltin(IV). Therefore, the systems investigated are completely new, and the results in this work must be considered as original, especially due to the statistical approach proposed and to the comparisons between the formation of the hetero-nuclear species respect to the homo-nuclear ones, also confirmed by the determination of their “extra-stability”.

As concern the hydrolysis of uranyl ion, for which many different speciation models have been proposed, we should say that the kind and the stability of species determined here are in good agreement with those already reported in our previous papers [18,19] and are consistent with results by other authors (see, for example, refs. [43,44]). A more detailed and critical analysis of literature data on this topic was already done in a previous paper [19].

4. Conclusions

Main conclusions on the formation of hetero-metal hydrolytic species can be summarized as follows:

(a) formation of hetero-polynuclear hydrolytic species between UO_2^{2+} and Cu^{2+} or $(C_2H_5)_2Sn^{2+}$ has been confirmed;

(b) dioxouranium(VI) and copper(II) form three mixed hydrolytic species [$(UO_2)Cu(OH)^{3+}$, $(UO_2)Cu(OH)_2^{2+}$ and $(UO_2)_2Cu(OH)_4^{2+}$], all those common to their simple speciation without the other cation;

(c) hydrolysis in dioxouranium(VI)/diethyltin(IV) system is dominated by first cation, because of the formation of seven mixed hydrolytic species [$(UO_2)(DET)(OH)_2^{2+}$, $(UO_2)(DET)(OH)^{3+}$, $(UO_2)_2(DET)(OH)_4^{2+}$, $(UO_2)(DET)_2(OH)_4^{2+}$, $(UO_2)_2(DET)(OH)_5^{+}$, $(UO_2)(DET)_2(OH)_5^{+}$ and $(UO_2)_2(DET)(OH)_7^{-}$] that are of the same kind of those formed by uranyl;

(d) hetero-metal hydrolytic species show an “extra-stability” respect to the homo-metal ones, higher than the statistically predicted one;

(e) the main contribution to the “extra-stability” is due to the enthalpic term;

(f) formation of mixed hydrolytic species causes a significant enhancement of the percentage of hydrolyzed metal cations.

These enhancements of hydrolysis mainly affect the speciation and the chemico-physical behavior of these metal cations. For example, also their solubility is modified, determining their release from sediments. As direct consequence, the bioavailability of these substances increases, with serious risks for the whole environment.

Acknowledgements

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