

# Determination of the stability constants of uranyl/polymer complexes by differential pulse polarography

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## Abstract

Differential pulse polarography (DPP) allows for the determination of the stability constants ( $K$ ) and the stoichiometry ( $n$ ) for the complexation of the  $\text{UO}_2^{2+}$  ion by various monomers and the parent polymers. The experimental observation is the shift of the totally reversible reduction wave  $\text{UO}_2^{2+} + \text{e}^- \rightleftharpoons \text{UO}_2^+$  toward more cathodic potentials when the complexing monomer or polymer is added to an uranyl nitrate aqueous solution. This shift is, however, much greater when the polymer is used rather than the monomer, in line with a higher stability of the complexes ( $K_{\text{polymer}} \gg K_{\text{monomer}}$ ). A theoretical stability scale of the polymers/ $\text{UO}_2^{2+}$  complexes was compared to an experimental one based on dynamic leaching tests. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Uranyl; Stability constants; Differential pulse polarography

## 1. Introduction

In previous papers, we reported on the complexation of uranyl ions by various polymers [1,2] and polymer composites [3] with the purpose to use these polymers for the treatment of low level activity liquid wastes in aqueous nitric solutions. Nevertheless, all the polymer/ $\text{UO}_2^{2+}$  complexes studied were soluble in water, unless crosslinked.

We proposed two original processes in order to make these complexes insoluble. The first one consisted of the addition of a polyanion, i.e. polystyrenesulfonate ( $\text{PSSO}_3^-$ ) or polystyrenecarboxylate ( $\text{PSCOO}^-$ ) [1,2] to the complex which precipitated as a neutral complex. In a second method,  $\text{UO}_2^{2+}$  complexes with a polyanion, such as polyacrylamidoglycolic acid (PAGA) or polyacrylamidomethylpropanesulfonic acid (PAMPS), were used as doping agents in insoluble polycationic polypyrrole [3].

With the practical treatment of radioactive wastes, in prospect, we analyzed the stability of the insoluble  $\text{UO}_2^{2+}$ /polymer complexes by continuous extraction in a Soxhlet apparatus. The quantitative determination of the uranium leached out was the criterion used to rank the polymers according to their efficiency.

In order to complete this rough analysis of the interactions between the  $\text{UO}_2^{2+}$  ions and various polymers, we

decided to measure the stability constants ( $K$ ) of the complexes by an electrochemical method, i.e. differential pulse polarography (DPP).

The association and dissociation rate constants  $k_a$  and  $k_d$ , in the complex equilibrium,  $\text{M} + n\text{L} \rightleftharpoons \text{ML}_n$ , are related to the stability constant by the following equation

$$K = k_a/k_d = \frac{C_{\text{ML}_n}}{C_{\text{M}}C_{\text{L}}^n},$$

where  $C_{\text{ML}_n}$ ,  $C_{\text{M}}$  and  $C_{\text{L}}$  are the bulk concentrations of the complex, the free ion and the ligand, respectively, and  $n$  is the stoichiometry of the complex. Different experimental techniques are reported in the scientific literature for the measurement of  $K$ . Nishide et al. [4] used a potentiometric technique in the case of various polyacrylic acid derivatives, whereas Kramer and Dunsch [5] paid attention to a voltammetric method, based on the shift of the reduction potential of the cation toward more cathodic values when ligand is regularly added to the cation solution. Actually, the shift of the half-wave ( $E_{1/2}$ ) polarographic potential is measured as mentioned in electrochemistry textbooks [6]. This electrochemical method is applicable whenever the electron transfer is reversible, as is the case for the  $\text{UO}_2^{2+} + \text{e}^- \rightleftharpoons \text{UO}_2^+$  equilibrium.

When organic ligands are considered, the electrochemical reaction can be perturbed by adsorption phenomena possibly responsible for potential shifts as pointed out by Kramer et al. [5]. Therefore, we made the choice to measure the potential shifts by DPP, because this technique allows to estimate the

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Table 1  
DPP experimental parameters

Drop time	0.5–1s
Pulse duration	50 ms
Pulse height	20–100 mV
Scan rate	2 mV/s
Drop size	0.5 mm <sup>2</sup>
Volume cell	10 ml
Reference electrode	Ag/AgCl (KCl 3 M)

reversibility of the electron transfer and to detect adsorption on the electrode. Although, the potential range in which no adsorption occurs could also be identified by alternating current polarography (ACP), this method is of delicate use.

In this paper, the stability constants of  $\text{UO}_2^{2+}$  complexes with water soluble monomers and parent polymers will be measured and compared to data extracted from leaching experiments. The ultimate purpose is to choose the system, which is most efficient to precipitate uranium from aqueous nitric wastes.

## 2. Experimental

### 2.1. DPP

This technique is fully described in the text-book by Bard and Faulkner [6]. For small pulses amplitudes, the potential at the maximum current (peak potential  $E_p$ ) is close to the  $E_{1/2}$  polarographic potential, such that  $E_p$  was measured in this study. For the transfer of a single electron ( $n = 1$ ) independently of any kinetic effect, the width of the peak at

half height (FWHM,  $\omega_{1/2}$ ) is ca. 90.4 mV at 25°C as stated in Eq. (1).

$$\omega_{1/2} = 3.52RT/nF = 90.4 \text{ mV} \quad (1)$$

$$(n = 1, T = 25^\circ\text{C and } \Delta E = 0)$$

In case of a reversible reaction with a soluble reduced species ( $\text{UO}_2^{2+}$ ), the peak current ( $i_p$ ) is proportional to the pulse height ( $\Delta E$ ) when the amplitudes are kept low, i.e. lower than or equal to 50 mV [6]. In order to check the possible occurrence of adsorption phenomena,  $i_p$  was measured at each potential shift for  $\Delta E$  ranging from 10 to 50 mV. Whenever the relationship between  $i_p$  and  $\Delta E$  was linear and FWHM was close to value around 90.4 mV, no adsorption was assumed to occur and the shift of  $E_p$  was used to calculate  $K$  according to Eq. (2) [7].

$$\Delta E_{1/2} = 0.059/Z(\log K + n \log[C_L]) \quad (2)$$

where  $\Delta E_{1/2}$  is the shift of the half-wave reduction potential,  $Z$  is the number of electrons exchanged in the reaction,  $n$  is the ligand to ion molar ratio,  $K$  is the stability constant of the complex and  $C_L$  is the ligand concentration expressed in mol/l.

The measurements were carried out with a PAR 273 potentiostat (EGG) connected with a 303-A static dropping mercury electrode (DME) and hanging dropping mercury electrode (HDME). The potential was referred to the classical standard Ag/AgCl electrode. The conducting salt was  $\text{NaNO}_3$  0.1 M. The experimental parameters are described in Table 1.

The DPP method relies on the reversibility of the  $\text{UO}_2^{2+}$  reduction, the reduced species  $\text{UO}_2^{2+}$  being stable in solution during the time-window of the measurement. Additional cyclic voltammetry (CV) on a hanging drop mercury

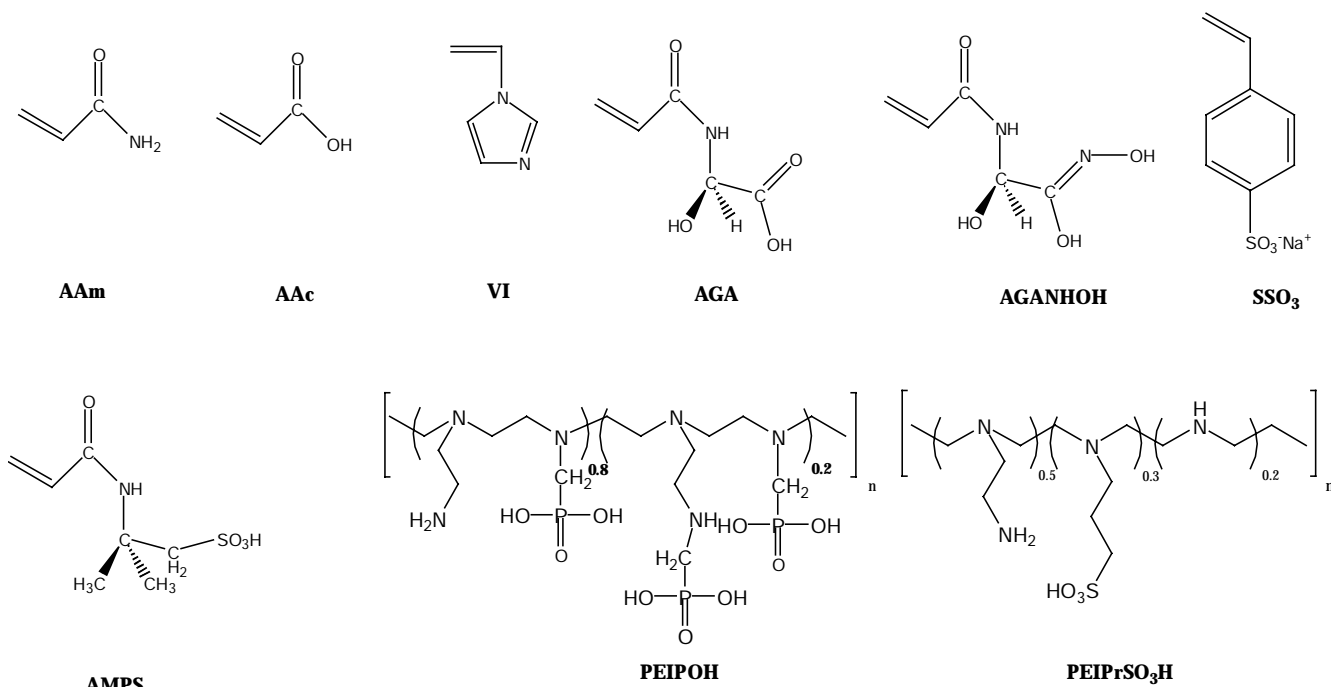


Fig. 1. Structure of monomers and PEI derivatives.

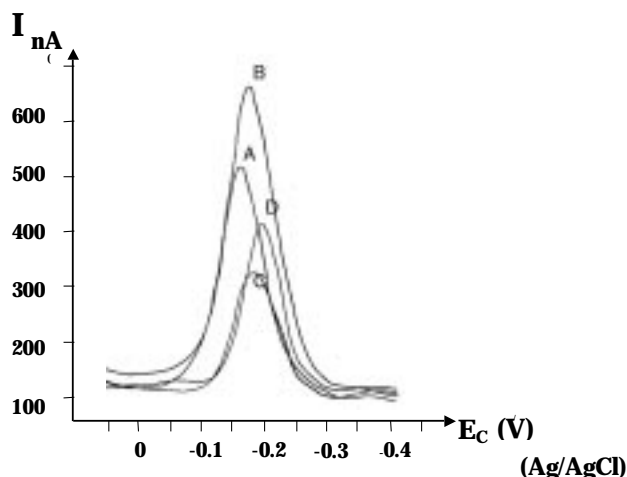


Fig. 2. DPP profiles ( $\Delta E = 50$  mV) for AGA/ $\text{UO}_2^{2+}$  complexes of different compositions: (A) pure  $\text{UO}_2^{2+}$ ; (B) AGA/ $\text{UO}_2^{2+} = 2$ ,  $\log[C_L] = -4$ ; (C) AGA/ $\text{UO}_2^{2+} = 30$ ,  $\log[C_L] = -2.82$ ; (D) AGA/ $\text{UO}_2^{2+} = 50$ ,  $\log[C_L] = -2.6$ .

electrode (HDME) showed that the  $i_{pa}/i_{pc}$  ratio ( $i_{pa}$  CV oxidation peak of  $\text{UO}_2^{2+}$  on reversal and  $i_{pc}$  CV reduction peak of  $\text{UO}_2^{2+}$ ) was close to 1 assessing the reversibility of the system under the experimental conditions used [6].

## 2.2. Synthesis of monomers and polymers

2-Acrylamidoglycolic acid monohydrate, AGA (26,049-5); 2-acrylamido-2-methyl-1-propanesulfonic acid, AMPS (28,273-1); acrylamide, AAm (14,857-1); vinylimidazole, VI (23,546-6) and acrylic acid, AAc (14,723-0) were supplied by Aldrich and used as received. AGA was also reacted with hydroxylamine [8],  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (25,558-0) Aldrich with formation of the hydroxamic acid derivative (AGANHOH).

The PAGA, PAMPS, PAAM, PAGANHOH and PVI polymers were prepared by classical radical polymerization initiated in water by 4,4'-azobis(4-cyanovaleric acid) [ $=\text{NC}(\text{CH}_3)(\text{CN})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ ] $_2$ , (ACVA), supplied by Acros organics (15259-0025). Two samples of polyacrylic acid (PAAc) of different molecular weight ( $M_w$ : 2000; Aldrich: 32,366-7) and ( $M_w$ : 750,000; Aldrich: 30,620-7) and poly(sodium styrenesulfonate) ( $\text{PSSO}_3^- \text{Na}^+$ ;  $M_w$ : 100,000; Acros: 22227-1000) were used. Polyethyleneimine (PEI;  $M_w$  50–60,000) was purchased from Acros (17857-1000). PEI was also reacted with chloropropanesulfonyl chloride (Aldrich: 12,519-9) in order to attach statistically propane sulfonic acid moieties to PEI (PEIPrSO $_3$ H) [9]. The sulfur content, measured by neutron activation analysis [10] (NAA), gave a molar ratio of propane sulfonate to ethyleneimine units of 0.2.

Phosphonic acid units were also attached to PEI by reaction with formaldehyde and phosphorous acid as reported by Smith et al. [11] (PEI:PEIPOH). The phosphorus content was also measured by neutron activation analysis, so leading to a  $\text{CH}_2\text{P}(\text{O})(\text{OH})_2$  to ethyleneimine molar ratio of 0.4

[10]. The structure of all the monomers and functionalized PEI is shown in Fig. 1.

## 2.3. Extraction tests

Dynamic extraction tests based on the MCC-5 Soxhlet test [12] were carried out with a water/polymer volume ratio of 50,000, for 24 h of non-stop extraction. The temperature of the condensed water was 65°C. The uranium content of water was measured by ICP analysis after extraction.

## 3. Results

### 3.1. Monomers/ $\text{UO}_2^{2+}$ complexes

A series of monomers, i.e. AGA, AGANHOH, AMPS, AAm, AAc, and VI was first investigated with a special attention to the monomer/ $\text{UO}_2^{2+}$  ratio from 0 to 50. The pH of the aqueous solution of  $\text{UO}_2^{2+}$  ( $[\text{UO}_2^{2+}] = 5 \times 10^{-5}$  M and  $[\text{NaNO}_3] = 0.1$  M) was 3.5. In all the cases, the pH did not increase upon the addition of an excess of ligands so that no hydroxide precipitated.

Typical DPP peaks for the AGA/ $\text{UO}_2^{2+}$  complex are shown in Fig. 2, the shift of  $E_{1/2}$  ( $\Delta E_{1/2}$  in V) being 28 mV when the monomer/ $\text{UO}_2^{2+}$  molar ratio is increased from 0 to 50. From these data, (only four curves were displayed for the sake of clarity), a plot of  $\Delta E_{1/2}$  vs.  $\log C_L$  has been drawn (Fig. 3). From the slope and the intercept of the straight line with the y axis, the stoichiometry of the complex ( $n$ , in Eq. (2)) and  $\log K$ , respectively, are calculated. In all these experiments,  $i_p$  is proportional to  $\Delta E$  (20, 50 and 100 mV) and the value of FWHM lies in the 110–120 mV range (Table 2), consistently with a reversible reaction. Actually  $\Delta E$  is never zero as supposed in Eq. (1), and the ohmic drop results in the broadening of the peak.

The values of the potential shifts and  $\log K$  are listed in Table 2, the experimental errors on the potential shift being 2% and from 0.5 to 11% for  $\log K$ .

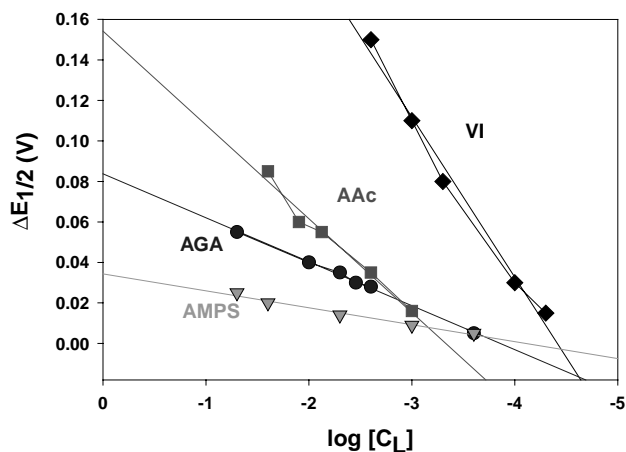


Fig. 3. Plot of  $\Delta E_{1/2}$  vs.  $\log[C_L]$  for the AGA/ $\text{UO}_2^{2+}$ , AMPS/ $\text{UO}_2^{2+}$ , AAc/ $\text{UO}_2^{2+}$  and VI/ $\text{UO}_2^{2+}$  complexes.

Table 2  
Monomer/ $\text{UO}_2^{2+}$  complex: stability constant and stoichiometry

Monomer	AGANHOH	VI	AAc	AGA	AAm	AMPS
$n$	2	1	2	3	2	6
$\log K$	5.1	4.5	3.5	1.7	1.0	0.6
FWHM (mV) Mon/ $\text{UO}_2^{2+} = 2$	95	110	95	98	105	102
FWHM (mV) Mon/ $\text{UO}_2^{2+} = 50$	115	120	115	110	120	120

The  $K$  values are rather low, in qualitative agreement with data reported in the literature for similar complexes [13].

### 3.2. Polymer/ $\text{UO}_2^{2+}$ complexes

The same analysis has been conducted for the parent polymers and for PEI, PEIPOH, PEIPrSO<sub>3</sub>H, and fully and partially protonated PVI, as well. PSSO<sub>3</sub><sup>-</sup>Na<sup>+</sup> has also been considered because this polymer will be used in one of the precipitation methods.

Three types of  $\Delta E_{1/2}$  vs.  $\log C_L$  plots have been observed.

#### 3.2.1. Linear dependence

Fig. 4 illustrates the linear dependence of  $\Delta E_{1/2}$  on  $\log C_L$  in the case of PAGA, PAGANHOH, PAAc, PAAm and PVI, whereas the DPP profiles are shown for PAGA in Fig. 5. Similar plots have been recorded for PVI-H<sup>+</sup> (50%) and PEIPOH. The values of  $n$  and  $\log K$  extracted from these plots are listed in Table 3.

It must be mentioned that the primary cause for the large decrease in the peak current intensity results from the decrease of the diffusion coefficient of the uranyl ion because of coordination to slowly diffusing macromolecule [5]. Comparison of  $\log K$  for complexing monomers (Table 2) and the parent polymers (Table 3), shows that the complexation stoichiometry remains unchanged. The stability constants for the  $\text{UO}_2^{2+}$  complexes increases whenever the polymer is substituted for the original monomer as result of a cooperative effect, as reported elsewhere [5].

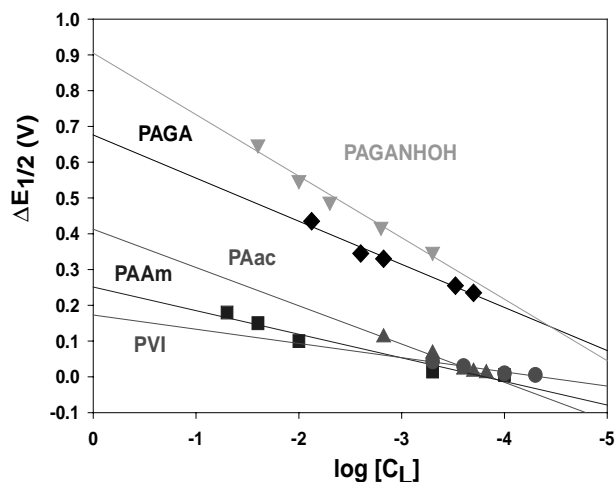


Fig. 4. Plot of  $\Delta E_{1/2}$  vs.  $\log [C_L]$  for several polymer/ $\text{UO}_2^{2+}$  complexes.

It is worth pointing out that  $\log K = 9.3$  for the PAAc/ $\text{UO}_2^{2+}$  system (Table 3), which is in agreement with  $\log K = 9.5$  determined by Nishide [4] by a completely different technique, i.e. potentiometric titration. As a rule,  $\log K$  reported in Table 3 are in line with data published about metallic ions/polymer complexes [14–17]. In case of PAAc, two samples of different molecular weight (200.000 and 1.000.000) have been analyzed and no difference in the complexation equilibrium has been observed.

When PVI is concerned, the 50% protonation has a deleterious effect on the complexation, which does not occur anymore whenever the protonation is complete, which emphasizes the key role of the free electron pair of the nitrogen atoms.

#### 3.2.2. Segmented dependence

There is a change in the slope of the  $\Delta E_{1/2}$  vs.  $\log C_L$  dependence whenever  $\text{UO}_2^{2+}$  is complexed by PAMPS, PEI and PEIPrSO<sub>3</sub>H, as illustrated in Fig. 6 for the  $\text{UO}_2^{2+}$ /PAMPS pair. This behavior is observed when the structure of the complex changes with the ligand concentration. So the breakdown in the slope reflects a change in the complexation constant. Eq. (2) allows  $K$  and  $n$  to be calculated for each linear segment. As an example, data collected in Fig. 6 lead to  $\log K = 0.9$  and  $n = 6$  at low  $C_L$  ( $-4.3 < \log [C_L] < -2.45$ ), and to  $\log K = 12.4$  and  $n = 60$  in the  $-2.45 < \log [C_L] < 0$  range. The breakdown in plot at  $[C_L] = 0.005$  M may be accounted for by a change from an extended conformation to a more compact structure [18] which restricts the access of the uranyl ions to part of

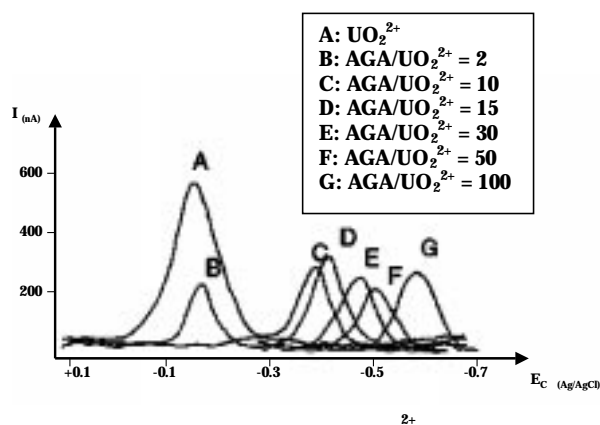


Fig. 5. DPP profiles for PAGA/ $\text{UO}_2^{2+}$  complexes.

Table 3  
Stability constant of polymer/ $\text{UO}_2^{2+}$  complexes

Polymer	PAGA NHOH	PAGA	PAMPS	PAAc	PEIPOH	PAAM	PEI	PEIPrSO <sub>3</sub> H	PVI	PVI-H <sup>+</sup> (50%)	PVI-H <sup>+</sup> (100%)	PSSO <sub>3</sub>
<i>n</i>	2	3	6	2	6 <sup>a</sup>	2			1		/	/
log <i>K</i>	16.3	14.6	0.9	9.3	7.5	7.1	2.2	1.6	4.7	3.4	/	/
[Mon]/[ $\text{UO}_2^{2+}$ ] = 10							(0–5)	(0–10)				
log <i>K</i>			12.4				4.5	5.1				
[Mon]/[ $\text{UO}_2^{2+}$ ] = 300							(5–20)	(10–300)				

<sup>a</sup> *n* = ethylene imine units/ $\text{UO}_2^{2+}$  ratio.

the complexing sites. This phenomenon could explain the unrealistic stoichiometry *n* = 60.

The complexation of uranyl by PEI and PEIPrSO<sub>3</sub>H is such that a curve fits the  $\Delta E_{1/2}$  on log  $C_L$  dependence. (Fig. 7). The ligand concentration  $C_L$  is expressed as equivalents of the  $\text{CH}_2\text{--CH}_2\text{N}$  units, because the nitrogen atom is supposed to be the site for the complexation of  $\text{UO}_2^{2+}$ . Although the curve indicates that the structure of the complex changes with the ligand concentration, we have tentatively compared the behavior of PEI and PEIPrSO<sub>3</sub>H from log *K* and *n* calculated for a dependence assumed to be linear in three ranges of  $C_L$  values

#### PEI

$$(-4.3 < \log[C_L] < -3.6) \quad n = 1/2; \log K = 2.2$$

$$(-3.6 < \log[C_L] < -3) \quad n = 1; \log K = 4.5$$

$$(-3 < \log[C_L] < -2.8) \quad n = 5; \log K = 17.1$$

#### PEIPrSO<sub>3</sub>H

$$(-4.3 < \log[C_L] < -3.3) \quad n = 0.35; \log K = 1.6$$

$$(-3.3 < \log[C_L] < -1.8) \quad n = 3.5; \log K = 5.1$$

$$(-1.8 < \log[C_L] < -1.65) \quad n = 12; \log K = 17.5$$

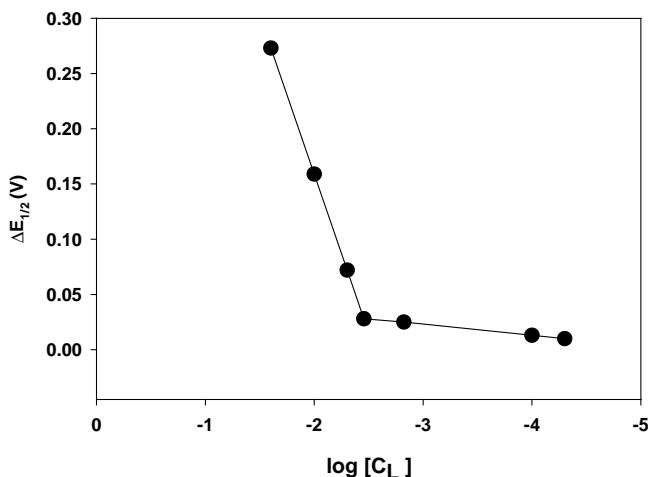


Fig. 6. Segmented plot of  $\Delta E_{1/2}$  vs.  $\log[C_L]$  for PAMPS/ $\text{UO}_2^{2+}$ .

Stoichiometry (*n*) smaller than 1 suggests that the approximation is not acceptable in the lower concentration range. It appears that *K* values are quite comparable for PEI and PEIPrSO<sub>3</sub>H, which supports that the sulfonate groups does not take part in the complexation of the uranyl and has no effect on the stability of the complexes. Only the stoichiometry of the complexation reaction is perturbed, in a possible connection with a change in chain conformation as result of the mutual electrostatic repulsion of the sulfonate groups.

Finally, when PEI is substituted by phosphoric acid groups (PEIPOH) the plot is linear, consistently with the complexation of  $\text{UO}_2^{2+}$  by the phosphonic acid groups.

#### 3.2.3. No shifts

The absence of complexation of the uranyl by sulfonate groups (see above) is confirmed by the analysis of PSSO<sub>3</sub>, which has no effect on the peak position.

#### 3.3. Precipitation of the polymer/ $\text{UO}_2^{2+}$ complexes

Two methods have been developed to make the uranyl/polymer complexes insoluble, i.e. addition of PSSO<sub>3</sub> and “in situ” polymerization of pyrrole. The permanency of the uranyl in the insoluble complexes has been investigated by leaching tests.

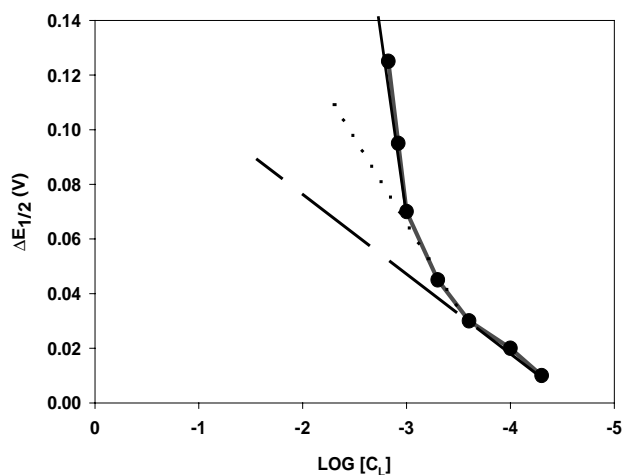
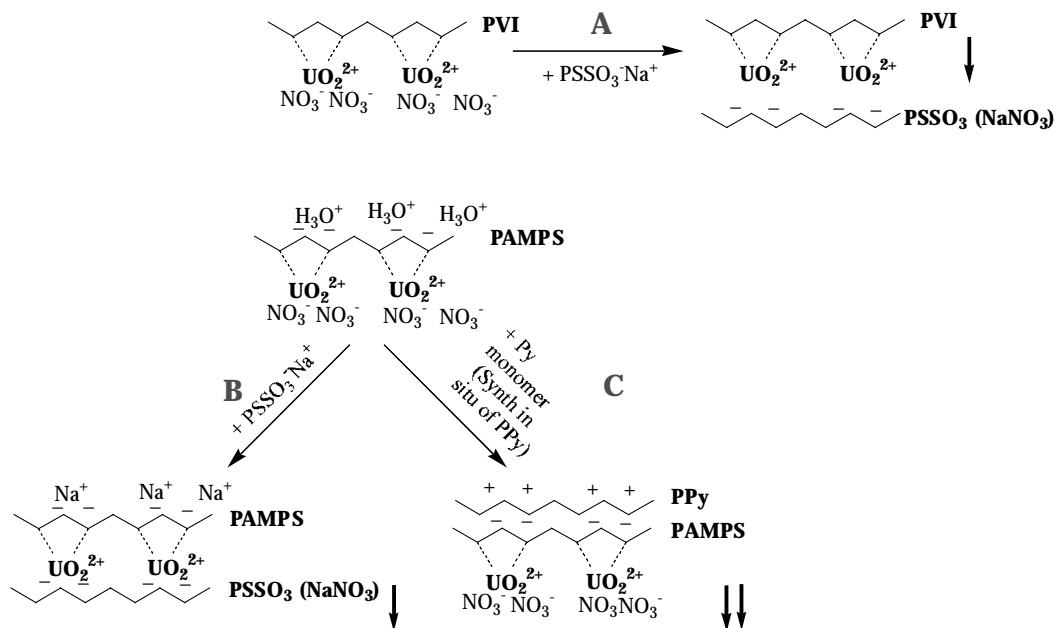


Fig. 7. Segmented plot of  $\Delta E_{1/2}$  vs.  $\log[C_L]$  for PEI/ $\text{UO}_2^{2+}$ .

Fig. 8. Precipitation of complexes by PPy and PSSO<sub>3</sub>.

### 3.3.1. Addition of PSSO<sub>3</sub>

The uranyl complexes precipitate as soon as added with PSSO<sub>3</sub> (Fig. 8a and b). Although PSSO<sub>3</sub> does not complex the  $\text{UO}_2^{2+}$  ions, it precipitates the  $\text{UO}_2^{2+}$ /polymeric ligand complex by formation of an interpolyelectrolyte complex (IPEC) [19] known for insolubility in water. Indeed, the  $\text{UO}_2^{2+}$  containing polymer is nothing but a polycation, whose nitrate counterions can be substituted by PSSO<sub>3</sub>. This typical situation prevails whenever the polymeric ligand is neutral (PAGANHOH, PAAm, PEI, PVI) as illustrated by Fig. 8a.

When the complexing polymer is a polyanion (PEIPrSO<sub>3</sub>H, PEIPOH, PAAc, PAGA and PAMPS), the complex formed with  $\text{UO}_2^{2+}$  is negatively charged. The exchange of the nitrate anions, by hydrophobic PSSO<sub>3</sub><sup>-</sup> is the driving force to interpolymer complexation and precipitation (Fig. 8b).

In all the experiments, the complexing monomer units were used in molar excess with respect to the stoichiometric amount of  $\text{UO}_2^{2+}$ , whereas PSSO<sub>3</sub> was also in molar excess with respect to the monomer unit of the complexing polymer (0.5–0.9 M) compared to the complexing polymer.

### 3.3.2. In situ polymerization of pyrrole

Polypyrrole (PPy) is insoluble in water and polycationic in the oxidized form. Therefore, negatively charged compounds can be incorporated as doping agents in this polymer as it is formed. All the complexes considered in this study which have a polyanionic backbone can thus be immobilized in the insoluble polypyrrole as schematized in Fig. 8c.

The amount of  $\text{UO}_2^{2+}$  released in pure water from the insolubilized complexes was measured in a Soxhlet

extractor in relation to the uranyl content. The data are listed in Table 4 for samples made insoluble by each of the two techniques (use of PSSO<sub>3</sub> and PPy, respectively).

In addition to the amount of uranyl which is leached from the insoluble complexes, Table 4 reports the *K* values characteristic of the soluble polymer/ $\text{UO}_2^{2+}$  complexes. It must be noted that this comparison is not straightforward, because the uranyl complexes have not been prepared under the same experimental conditions, e.g.  $[\text{UO}_2^{2+}] = 5 \times 10^{-5}$  M when *K* is measured and  $5 \times 10^{-2}$  M when the complexes are precipitated and tested for stability. Moreover, *K* is measured at room temperature and the leaching

Table 4  
Dynamic leaching test

Uranyl complexes	% of $\text{UO}_2^{2+}$ released in leaching water <sup>a</sup>	log <i>K</i> <sup>b</sup>
PVI/PSSO <sub>3</sub> <sup>-</sup> / $\text{UO}_2^{2+}$	45	4.7
PEI/PSSO <sub>3</sub> <sup>-</sup> / $\text{UO}_2^{2+}$	55	6.7
PEIPrSO <sub>3</sub> H/PSSO <sub>3</sub> <sup>-</sup> / $\text{UO}_2^{2+}$	54	6.7
PAAm/PSSO <sub>3</sub> <sup>-</sup> / $\text{UO}_2^{2+}$	62	7.1
PEIPOH/PSSO <sub>3</sub> <sup>-</sup> / $\text{UO}_2^{2+}$	42	7.5
PAAc/PSSO <sub>3</sub> <sup>-</sup> / $\text{UO}_2^{2+}$	53	9.3
PAMPS/PSSO <sub>3</sub> <sup>-</sup> / $\text{UO}_2^{2+}$	41	13.3
PAGA/PSSO <sub>3</sub> <sup>-</sup> / $\text{UO}_2^{2+}$	19	14.6
PAGANHOH/PSSO <sub>3</sub> <sup>-</sup> / $\text{UO}_2^{2+}$	9	16.3
PPy/PAGA/ $\text{UO}_2^{2+}$	2	14.6
PPy/PAMPS/ $\text{UO}_2^{2+}$	6	13.3
PPy/PEIPOH/ $\text{UO}_2^{2+}$	10	7.5
PPy/PEIPrSO <sub>3</sub> H/ $\text{UO}_2^{2+}$	26	6.7

<sup>a</sup> Wt % of  $\text{UO}_2^{2+}$  leached with respect to the initial amount in the insoluble complex.

<sup>b</sup> For the soluble polymer/ $\text{UO}_2^{2+}$  complex.

Table 5  
Dynamic leaching test

Uranyl complexes	Percent of $\text{UO}_2^{2+}$ released in leaching water <sup>a</sup>	$\log K^b$
PEI/PSSO <sub>3</sub> <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	55	6.7
PEIPrSO <sub>3</sub> H/PSSO <sub>3</sub> <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	54	6.7
PEIPOH/PSSO <sub>3</sub> <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	42	7.5
PAMPS/PSSO <sub>3</sub> <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	41	13.3
PAGA/PSSO <sub>3</sub> <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	19	14.6
PAGANHOH/PSSO <sub>3</sub> <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	9	16.3
PAAm/PSSO <sub>3</sub> <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	62	7.1
PAAc/PSSO <sub>3</sub> <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	53	9.3
PVI/PSSO <sub>3</sub> <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	45	4.7

<sup>a</sup> Wt % of  $\text{UO}_2^{2+}$  calculated with respect to the initial amount in the component.

<sup>b</sup> Corresponding to the complex polymer/ $\text{UO}_2^{2+}$  without PSSO<sub>3</sub><sup>-</sup>.

tests are conducted at ca. 65°C. Finally, the precipitation method used can perturb the structure of the originally soluble complexes (Table 5).

Nevertheless, there is a qualitative agreement between the stability scales based on  $\log K$  and the leaching tests, respectively, at least when the polymeric ligands are classified as follows:

(i) *Acrylic and acrylamido polymers*. In this class of ligands, Table 4 shows that increasing amounts of uranyl are leached out from the insoluble complexes parallel to decreasing complexation constants. Therefore, the efficiency of the ligands decreases in the following order PAGANHOH > PAGA > PAMPS > PAAc > PAAm.

(ii) *PEI polymers*. The same conclusion holds, and the ranking of the polymeric ligands is PEIPOH > PEI = PEIPrSO<sub>3</sub>H.

(iii) *PVI*. Although PVI has the lowest  $\log K$  value (i.e. 4.7) the leaching tests do not rank it as the worst ligand. It must be noted that the NAA analysis of the PVI/ $\text{UO}_2^{2+}$  complex and the ICP analysis of the calcinated complex led to an uranium content such that the PVI/ $\text{UO}_2^{2+}$  ratio should be ca. 5, which is in line with  $n = 5$  previously determined by UV spectroscopy [1]. The difference noted in the experimental value of  $n$ , depending on the method used could originate from a difference in the concentration range used in the DPP experiments ( $[\text{UO}_2^{2+}] = 5 \times 10^{-5} \text{ M}$ ) and the UV measurements ( $[\text{UO}_2^{2+}] = 5 \times 10^{-3} \text{ M}$ ). Nevertheless, this situation was the same whatever the complexing polymer. Therefore, a change in the coordination of the uranyl when passing from the monomer to the polymer might be responsible of the observed discrepancy. The higher hydrophobicity of PVI compared to PAAc and PAAm could also be part of the explanation.

From Table 4, it is clear that the stability of the complexes

made insoluble by PPy is much higher compared to the complexes precipitated by PSSO<sub>3</sub>.

#### 4. Conclusions

It appears from Table 2 that the stability of the AGANHOH/ $\text{UO}_2^{2+}$  complex is one order of magnitude higher than that one of the AMPS/ $\text{UO}_2^{2+}$  complex, as result of the well-known complexing properties of the hydroxamic acid. Although VI is a good ligand, as was claimed in a Westinghouse patent [20], the fully protonated polymer has no complexing properties.

As expected [5] the calculated  $K$  value is higher for each polymer than for the parent monomer, except for the VI/PVI pair. Without a precise knowledge of the structure of the complexes, only very tentative explanation could be proposed. One may merely point out that the structure of the VI/ $\text{UO}_2^{2+}$  complex ( $n = 1$ , Table 2) seems different compared to the other monomers ( $n = 2$  and more; Table 2). Once again with the exception of VI and PVI, there is a parallelism in the complex stability estimated from the  $K$  values and the leaching tests.

Finally the most stable complexes are based on PAGANHOH, PAGA and PAMPS. The two PAGA and PAMPS polyanions have the advantage to be used as doping agents for PPy and to form insoluble composites suited to the extraction of  $\text{UO}_2^{2+}$  from liquid wastes [3]. When incorporated in PPy matrixes, these two polymers show the same relative stability against dynamic leaching.

The two original insolubilization techniques (PSSO<sub>3</sub> and PPy) proposed in this work are complementary because neutral complexing polymers can be precipitated by PSSO<sub>3</sub>, which is impossible in the PPy based approach, the polycationic PPy being doped only by polyanions.

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