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Palladium(II) Complexes of Aminopolycarboxylic Ligands in Aqueous Solution

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S *Supporting Information*

ABSTRACT: The binding capacity of five aminopolycarboxylic ligands (APCs) [nitrilotriacetate (NTA), ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (EDTA), (*S*,*S*)-ethylenediamine-*N*,*N*′-disuccinic acid (S,S-EDDS), diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetate (DTPA), and triethylenetetraamine-*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexaacetate (TTHA)] toward the palladium(II) ion was studied by potentiometric titrations (ISE-H^+ electrode) in $NaNO_3$ and in $NaClO_4$/NaI (at different molar ratios) solutions and by spectrophotometric titrations (only in $NaClO_4$), at $I = 0.1\ mol\cdot kg^{-1}$ and at $T = 298.15$ K. The high stability of Pd^{2+}-complexones species inhibits the formation of sparingly soluble hydroxo species until pH 11. In the pH range investigated and at the Pd^{2+}/APC ratios used in the experiments (1/1−1/4), all of the complexones form with palladium(II) only protonated or unprotonated mononuclear species and the monohydroxo species Pd(APC)(OH). As consequence of the ligand structure and of the number of amino and carboxylic groups involved in the coordination, the stability of palladium(II)−APC species follows the trend: TTHA > DTPA > EDTA > S,S-EDDS > NTA; for example, the log K_{PdL} is 37.00, 36.31, 23.60, 23.07, and 17.82 for L = TTHA, DTPA, EDTA, S,S-EDDS, and NTA, respectively. A critical evaluation of literature evidenced the big discrepancies in stability data and also in the speciation models proposed by different authors. A comparison of the sequestering capacity of complexones toward palladium(II) and other divalent metal ions was done by using stability data from this work and literature ones.

1. INTRODUCTION

The more and more increasing use of catalytic converters to reduce the dangerous NO_x and CO emission in the atmosphere by vehicle traffic produces a corresponding increase of palladium in the environment,[1] this metal, together with platinum and rhodium (the so-called platinum group elements, PGE), being the main component of the catalytic converters in the automobiles. Among the PGE, elemental palladium seems to be the most hazardous one because it can be easily and quickly oxidized to palladium(II) when put in contact with soil.[2,3] The presence of palladium oxidized forms is of great concern since an increase of the mobility and the bioavailability of this element in the environment and an easier uptake by plants, animals, and humans can occur. On the other hand, the environmental presence of palladium as palladium(II) ion could be an advantage in setting-up soil and water remediation processes if appropriate chelating agents for this metal ion removal are found.

Since more than 50 years, the most used chelating agents are the (poly)amino (poly)carboxylic ligands (APCs, also called "complexones").[4] APCs, which include at least 20 different molecules, are employed in several application fields, for example: (i) in agriculture to modulate the metal absorption by roots and to remove metals from contaminated sites,[5,6] (ii) in medicine for chelation therapy[7] and radio diagnostic analysis,[8] (iii) in water treatment to remove undesirable and toxic metal ions,[9] and (iv) in all of the other industrial processes (photography, cosmetics, pulp and paper, detergents, food, metal plating, etc.) where metal ions must be absent (or present at negligible concentration) in the final products.[10] The most used complexones are nitrilotriacetate (NTA), ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (EDTA), and diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetate (DTPA) as documented by their utilization in Europe of about 200 000 tons in the year 2000.[4]

The great success of complexones as metal chelating agents is due to the very high stability of the complex species formed in solution which allows the considerable reduction of the activity of free metal ions in solution. Almost all metal ions form with APCs complex species with different stability, as documented by several articles and compilations where critically evaluated values of stability constants are also reported.[11−13] Unfortunately, few data are reported in the literature on the stability of the species formed by interaction of complexones with platinum group elements (PGE, platinum, palladium, rhodium), and no critical value is reported for the relative stability constants. The lack of stability data for complex species formed in these systems is in contrast with the increase of the worldwide demand of PGEs.

With the aim to evaluate the possibility of using complexones as chelating agents for the palladium(II) ion in aqueous solution, we report here stability data for the interaction of Pd^{2+} with the following APC ligands: NTA, (*S*,*S*)-ethylenediamine-*N*,*N*′-disuccinic

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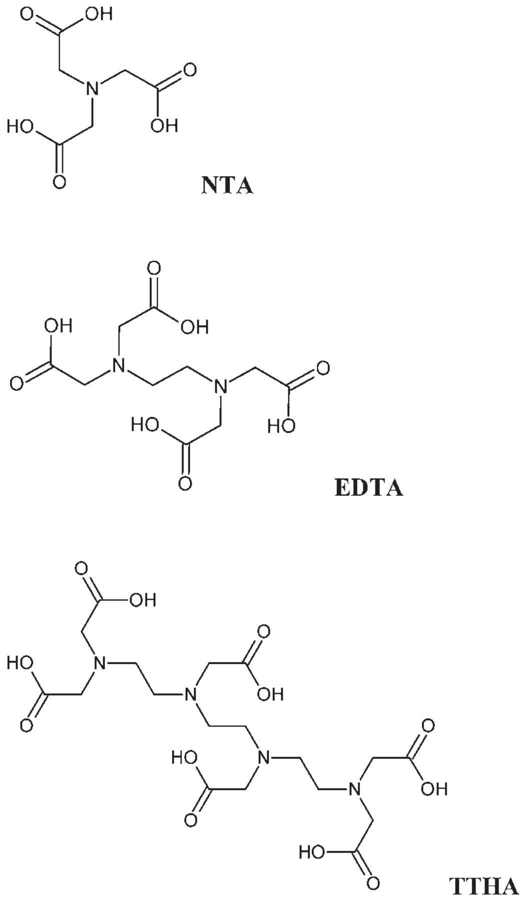

Figure 1. Structure of aminopolycarboxylic ligands.

acid (S,S-EDDS), EDTA, DTPA, and triethylenetetraamine-*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexaacetate (TTHA) (structures are shown in Figure 1).

The choice of these complexones depends on the following factors: (i) NTA, EDTA, DTPA, and TTHA were chosen to evaluate the influence of the increasing number of amino and carboxylic donor groups on the stability of complex species; (ii) the S,S-EDDS was chosen because it has been shown to be the most biodegradable among the complexones. This is of particular relevance from the environmental point of view. In fact, most of complexones have low biodegradability and maintain their structure and their reactivity unaltered after they have been largely used in metal removal processes. As a consequence some undesirable effects can be produced, such as (i) remobilization of metal ions from sediments into the natural waters (lakes, rivers, seawaters, etc.); (ii) changing of uptake of essential and toxic metal ions by plants and other living organisms.[4] Results obtained by bio and/or photo degradation tests, expressed as readily biodegradability indices (RBI), show that EDTA is the less biodegradable APC, while the highest biodegradability is shown by S,S-EDDS.[14−17] The S,S-EDDS is one of the three stereoisomers of EDDS (S,S-EDDS, S,R/R,S-EDDS, and R,R-EDDS), which, as can be seen from Figure 1, has two chiral carbons in the molecule. S,S-EDDS is produced by microorganisms, and for the first time it has been isolated as a product of the metabolism of the *Amycolatopsis orientalis* actinomycete in soils.[17−19] Among the three stereoisomers only S,S-EDDS is almost completely biodegradable as confirmed by several tests used to evaluate the permanence time of polymeric materials in the environment.[20,21] It is selectively produced by the reaction between 1,2 dibromomethane and L-aspartic acid.[15,22,23] Since it shows high biodegradability and no toxicity, S,S-EDDS can be considered an environmentally friendly chelating agent that could substitute the other APCs in all of the application fields.

For the above reasons S,S-EDDS was included among the APCs to be considered as chelating agents for the palladium(II) ion. Investigations were performed to assess the complex species formed in each Pd^{2+}−APC system and to determine the relative stability constants with the aim to quantitatively define the sequestering capacity of each APC ligand toward the palladium ion in aqueous solution.

From the analysis of the literature stability constant values for the NTA, (S,S)-EDDS, EDTA, DTPA, and TTHA−Pd^{2+} complex species formation[24−29] (see Table 1), a discrepancy emerges probably due to the use of different techniques in determining the value of the stability constant of Pd(APC) species which is too high to be evaluated only by the classical potentiometric (proton displacement) technique.

To overcome the difficulty in the calculation of ML species stability constants, the results obtained from two series of ISE-H^+ potentiometric titrations (in $NaNO_3$ and in mixed $NaClO_4$/NaI ionic medium) were combined with those obtained from ISE-H^+ potentiometric/spectrophotometric titrations (in $NaClO_4$). Measurements were carried out at $T = 298.15$ K and at ionic strength $I = 0.1\ \mathrm{mol\cdot kg^{-1}}$ in the different (single and mixed) ionic media (details on the experimental conditions used are reported in the

Table 1. Literature log β Values [a] of Pd^{2+}—L Species (L = NTA, S,S-EDDS, EDTA, DTPA or TTHA) in Different Ionic Media, Ionic Strengths, and Temperatures

medium	I[b]	T[c]	log β_{110}	log β_{111}	log β_{112}	log β_{113}	log β_{114}	ref
Pd^{2+}—TTHA								
$NaClO_4$	0.5	25	18.73	25.65	28.55	31.05	33.50	25
				(6.92)	(2.90)	(2.50)	(2.45)	
Pd^{2+}—DTPA								
$NaBr/NaClO_4$	0.2/0.8	20	29.7[d]	33.2	36.26	38.99	41.29	29[e]
				(3.50)	(3.06)	(2.73)	(2.3)	
Pd^{2+}—EDTA								
$NaClO_4$	1	20	24.5[d]	27.51	29.82	30.72		29[f]
				(3.01)	(2.31)	(0.9)	(<0)	
ClO_4^-	0.2	25	18.5					26
not reported	0.1	25	26.4					28
$NaClO_4$	0.2	21	25.6					27
Pd^{2+}—S,S-EDDS								
KNO_3	0.1	30	13.6					24
Pd^{2+}—NTA								
$NaClO_4$	1	20	17.1	19.58	23.7[g]			29
				(2.48)	(6.6)[g]			

[a] log β_{pqr} refers to eq 1; log K_{pqr} reported in parentheses refers to eq 2 [b] In $mol \cdot L^{-1}$. [c] In °C. [d] log β_{110} value calculated in $NaBr_{aq}$ at $I = 1\ mol \cdot L^{-1}$. [e] Other log K_{plr} values at different $NaBr/NaClO_4$ ratio are reported by authors. [f] log β_{110} = 25.5 in KBr, at $I = 1\ mol \cdot L^{-1}$ and T = 293.15 K was reported by authors. [g] log β_{120} and log K_{120}.

experimental section). The stability constants determined here are discussed and compared with those reported in the literature. The stability data obtained for the species formed in the different Pd^{2+}—APC systems allowed us to assess the different sequestering capacity of the five complexones used toward the palladium(II) ion in the pH range investigated. To this end the pL_{50} parameter, already tested successfully for other metal—ligand systems,[30−33] was used. This parameter gives quantitative information on the sequestration capability of a ligand toward metal ions at fixed experimental conditions of pH and ionic strength. Details on the meaning and calculation of pL_{50} are reported in the sequestering capacity section. In our opinion the pL_{50} parameter can be used as a valid alternative to the speciation efficiency indices (SEI) already proposed for industrial purposes.[10,34]

2. MATERIALS AND METHODS

2.1. Chemicals. Palladium(II) nitrate dihydrate (by Sigma-Aldrich, purum) stock solutions were prepared by dissolving the weighed salt in 0.1 $mol \cdot kg^{-1}$ nitric acid. The palladium concentration was checked by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique against $Pd(NO_3)_2$ standard solutions (Fluka)[35] or gravimetrically using the dimethylglyoxime method.[36] NTA, S,S-EDDS, DTPA, and TTHA were used in their acidic forms; EDTA was used as disodium salt. All ligands were supplied by Fluka with analytical grade purity, and their purity was checked potentiometrically by alkalimetric titrations. $NaNO_3$, $NaClO_4$, and NaI solutions were prepared by weighing pure salts (Fluka) after drying in an oven at 383.15 K for 2 h. Nitric acid, perchloric acid, and sodium hydroxide solutions were prepared by diluting concentrated ampules (Riedel de Haën) and were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. NaOH solutions were preserved from atmospheric CO_2 by means of soda lime traps. All solutions were prepared with analytical grade water (R = 18 MΩ) using grade A glassware.

2.2. Potentiometric Apparatus and Procedure. Potentiometric titrations were carried out at (298.15 ± 0.1 K) using an apparatus consisting of a model 713 Metrohm potentiometer, equipped with a combined glass electrode (Ross type 8102, from Orion) and a model 765 Metrohm motorized buret. The estimated accuracy was ± 0.2 mV and ± 0.003 mL for electromotive force (emf) and titrant volume readings, respectively. The apparatus was connected to a PC, 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 presaturated N_2 was bubbled through the purified solution to exclude O_2 and CO_2 inside. Five series of potentiometric titrations were performed to study the formation of the complex species of palladium(II) with the complexones investigated (NTA, S,S-EDDS, EDTA, DTPA, and TTHA) in $NaNO_3$ and in mixed $NaClO_4$/NaI ionic medium, at $I = 0.1\ mol \cdot kg^{-1}$. In the case of measurements in mixed ionic medium, several $NaClO_4$/NaI ratios were used. In all titrations, the titrand solutions contain known amounts of palladium(II) nitrate, aminopolycarboxylic ligand, supporting electrolyte, and the necessary amount of HNO_3 or $HClO_4$ to acidify the solution at pH ≈ 1. In each series of titrations, a volume of 25 mL of the titrand solution was titrated with standard NaOH. Details of the experimental measurements are reported in Table 2. About 80 to 100 points were collected for each titration, and the equilibrium state during titrations was checked by monitoring the time necessary to reach equilibrium (several titrations were carried out with different equilibration periods ranging between (10 and 60) s per data point) and by performing back-titrations. For each experiment, independent titrations of strong acidic solution with standard base were carried out under the same temperature, medium, and ionic strength conditions as in the systems to be investigated, with the aim of determining the electrode potential (E^0) and acidic junction potential ($E_j = j_a\,[\mathrm{H}^+]$).

2.3. Spectrophotometric Apparatus and Procedure. The UV–vis spectra were recorded in the wavelength range (250 to 400) nm, using a spectrophotometer (Beckman, DU 640B) equipped with a peristaltic pump (Velp Scientifica, type SP 311) and a flow cell (Hellma, 176.000-QS) with a 1 cm optical path length. The spectrophotometer was connected to a PC for the acquisition of the spectra. The combined potentiometric and spectrophotometric titrations were carried out by using the same cell and potentiometric apparatus described in the previous paragraph. A volume of 40 mL of the solutions containing the complexone, palladium(II) ion, perchloric acid, and sodium perchlorate at $I = 0.1\ \mathrm{mol \cdot kg^{-1}}$ was titrated with a standard NaOH solution to obtain the maximum absorbance of each predominant species, according to the preliminarly determined speciation diagrams of the systems. Details of experimental measurements are reported in Table 2.

Table 2. Experimental Conditions for Potentiometric[a] and Spectrophotometric Measurements at $I = 0.1\ \mathrm{mol \cdot kg^{-1}}$ and $T = 298.15$ K

technique	ionic medium	C_{Pd}[b]	C_{L}[b]	pH range
		NTA		
potentiometry (ISE-H$^+$)	$\mathrm{NaNO_3}$	0.8–1.0	1.0–2.2	2.05–11.10
spectrophotometry	$\mathrm{NaClO_4}$	0.4	1.6–2.5	1.40–11.02
		S,S-EDDS		
potentiometry (ISE-H$^+$)	$\mathrm{NaNO_3}$	0.5–1.0	1.5–2.2	2.10–11.05
potentiometry (ISE-H$^+$)	$\mathrm{NaClO_4/NaI}$[c]	0.4–0.5	1.9–2.5	3.79–10.59
spectrophotometry	$\mathrm{NaClO_4}$	0.5	1.6–2.0	1.44–10.93
		EDTA		
potentiometry (ISE-H$^+$)	$\mathrm{NaNO_3}$	0.7–1.0	3.0–5.0	2.37–11.03
potentiometry (ISE-H$^+$)	$\mathrm{NaClO_4/NaI}$[c]	0.4–0.5	2.0–3.0	5.35–11.08
spectrophotometry	$\mathrm{NaClO_4}$	0.4	0.8–1.5	1.52–9.81
		DTPA		
potentiometry (ISE-H$^+$)	$\mathrm{NaNO_3}$	0.8–1.0	3.0–5.0	2.27–11.09
potentiometry (ISE-H$^+$)	$\mathrm{NaClO_4/NaI}$[c]	0.4–0.5	2.0–2.1	5.13–11.03
spectrophotometry	$\mathrm{NaClO_4}$	0.5	1.5–2.0	1.53–10.98
		TTHA		
potentiometry (ISE-H$^+$)	$\mathrm{NaNO_3}$	0.4–0.5	1.0–2.0	2.56–10.92
potentiometry (ISE-H$^+$)	$\mathrm{NaClO_4/NaI}$[c]	0.5–0.6	1.5–2.0	4.74–11.15
spectrophotometry	$\mathrm{NaClO_4}$	0.4	1.3–1.6	1.60–11.07

[a] 80 to 100 points for each measurement. [b] Analytical concentration in $\mathrm{mmol \cdot kg^{-1}}$; [c] At different ratios.

2.4. Calculations. The nonlinear least-squares computer program ESAB2M[37] was used for the refinement of all parameters of the acid–base titration (E^0, K_w, liquid junction potential coefficient, j_a, analytical concentration of reagents). The BSTAC and STACO[38] and HYPERQUAD 2006[39] computer programs were used in the calculation of complex formation constants from potentiometric titrations. UV–vis spectra were analyzed by the HYPSPEC[40] program, which allows us to calculate stability constants and the molar absorbance of each absorbing species, using as input the experimental absorbances, analytical concentrations of reagents, and the chemical model proposed. The ES4ECI[41] program was used to draw speciation diagrams and to calculate species formation percentages. The LIANA[42] program was used to fit different linear and nonlinear functions.

Overall and stepwise protonation constants of complexones, hydrolysis constants of palladium(II) ion and formation constants of $\mathrm{Pd^{2+}}$–APC complex species are given according to the equilibria 1 and 2 ($p = 0$ for protonation; $q = 0$ and r negative for hydrolysis):

$$p\mathrm{Pd}^{2+} + q\mathrm{L}^{z-} + r\mathrm{H}^{+} = \mathrm{Pd}_p\mathrm{L}_q\mathrm{H}_r^{(qz-2p-r)-} \qquad \beta_{pqr} \tag{1}$$

$$\mathrm{Pd}_p\mathrm{L}_q\mathrm{H}_{r-1}^{(z-r+1)-} + \mathrm{H}^{+} = \mathrm{Pd}_p\mathrm{L}_q\mathrm{H}_r^{(qz-2p-r)-} \qquad K_{pqr} \tag{2}$$

where $\mathrm{L}^{z-} = \mathrm{NTA}^{3-}$, S,S-$\mathrm{EDDS}^{4-}$, EDTA^{4-}, DTPA^{5-}, or TTHA^{6-} and negative r values stand for OH^-. Formation constants, concentrations, and ionic strengths are expressed in the molal ($\mathrm{mol \cdot kg^{-1}}$) concentration scale [formation constants in molar ($\mathrm{mol \cdot L^{-1}}$) concentration scale are reported as supplementary data; in many cases the difference between the concentrations in the two scales (molar and molal) is not significant and within the experimental errors].

Table 3. Protonation Constants[a] of NTA,[b] S,S-EDDS, EDTA,[c] DTPA,[b] and TTHA[b] in $\mathrm{NaNO_3}$, at $I = 0.1\ \mathrm{mol \cdot kg^{-1}}$ and $T = 298.15$ K

ligand	$\log \beta_{011}$	$\log \beta_{012}$	$\log \beta_{013}$	$\log \beta_{014}$	$\log \beta_{015}$	$\log \beta_{016}$	$\log \beta_{017}$
TTHA	10.492	19.983	26.082	30.019	32.650	34.822	36.371
		(9.491)[d]	(6.099)	(3.937)	(2.631)	(2.172)	(1.549)
DTPA	10.126	18.636	22.83	25.536	27.666	28.776	
		(8.510)	(4.19)	(2.706)	(2.130)	(1.110)	
EDTA	9.36	15.451	18.163	20.306			
		(6.091)	(2.712)	(2.143)			
S,S-EDDS	9.89 ± 0.02	16.87 ± 0.02	20.82 ± 0.02	23.87 ± 0.02	26.08 ± 0.04		
		(6.98)	(3.95)	(3.05)	(2.21)		
NTA	9.327	11.868	13.573	14.885			
		(2.541)	(1.705)	(1.312)			

[a] $\log \beta_{0qr}$ refers to eq 1 and are expressed in molal ($\mathrm{mol \cdot kg^{-1}}$) concentration scale; [b] From ref 45. [c] From ref 44. [d] $\log K_{0qr}$ in parentheses refers to eq 2.

Table 4. Iodo Complexes Species of the Palladium(II) Ion in $NaClO_4$/NaI Mixed Ionic Medium, at T = 298.15 K

ionic medium	I mol·kg^{-1}	log K_{PdI}	log β_{PdI_1}	log β_{PdI_3}	log β_{PdI_4}
$NaClO_4$/NaI	1	6.06[a]	22[a]	25.7[a]	28.2[a]
$NaClO_4$/NaI	0.1	6.37[b]	22.43[b]	26.23[b]	28.58[b]

[a] Reference 46. [b] This work (calculated).

3. RESULTS AND DISCUSSION

In building the complexation models for all investigated palladium(II)−APC systems, the protonation of APC ligands (NTA, S,S-EDDS, EDTA, DTPA, and TTHA) and the hydrolysis of palladium(II) ion were always taken into account.

3.1. Protonation of APC Ligands. The protonation constants of APCs are in general strongly dependent on the ionic medium as largely discussed in a previous article.[43] The protonation constants of NTA, EDTA, DTPA, and TTHA used here (see Table 3) are literature data;[44,45] the protonation constants of S,S-EDDS were determined in this work. All of the protonation constants used in this work are reported at I = 0.1 mol·kg^{-1} (Na^+ ionic medium) and at T = 298.15 K.

3.2. Hydrolysis of Palladium(II) and Interaction with the Anions of the Supporting Electrolyte. The high stability of Pd^{2+}−APC complex species, in the pH range investigated, strongly inhibits the hydrolysis of palladium(II) ion; nevertheless, for accuracy, the hydrolysis constants of Pd^{2+} ion were considered in the speciation models of all of the investigated systems.

The values of the conditional hydrolysis constant of the $Pd(OH)^+$ species, the most important hydroxo species of palladium(II) ion, log $K_{Pd(OH)}$ = −2.08 in $NaClO_4$ (considered by the majority of authors as a noninteracting medium) and log $K_{Pd(OH)}$ = −2.22 in $NaNO_3$ ionic media (I = 0.1 mol·kg^{-1}, T = 298.15 K) were taken from literature (ref 32 and references therein).

The interaction of the palladium(II) ion with the anions of the supporting electrolytes was also taken into account. The formation constant values of the PdI_n species reported by Elding and Olsson[46] at I = 1 mol·L^{-1} (see Table 4) were used in the calculations to obtain formation constants at I = 0.1 mol·kg^{-1} by using the extended Debye−Hückel type eq 3:

$$\log K = \log {}^{T}K - z \cdot 0.51 I^{1/2}(1 + 1.5 I^{1/2})^{-1} + CI + DI^{3/2} \tag{3}$$

where C and D are empirical parameters and $z^* = \Sigma(\text{charges})^2_{\text{reactants}} - \Sigma(\text{charges})^2_{\text{products}}$. K is the formation constant and ${}^{T}K$ the formation constant at infinite dilution. In Na^+ media, according to previous results (unpublished results from these laboratories), the values $C = 0.067z^*$ and $D = -0.04z^*$, can be used. In the mixed perchlorate−iodide medium the log $K_{Pd(OH)}$ obtained in $NaClO_4$, at the corresponding ionic strength, was considered.

3.3. Complex Species Formation in the Pd^{2+}−APC Systems. The complex species formation refers to equilibria 1 and 2. In the calculations, the formation of simple, protonated, and mixed hydroxo species has to be considered, under the experimental concentrations used ($0.5 \leq C_{Pd}$/mmol·kg^{-1} ≤ 1 and $1 \leq C_{APC}$/mmol·kg^{-1} ≤ 5) and in the pH range (2 to 11.5) investigated.

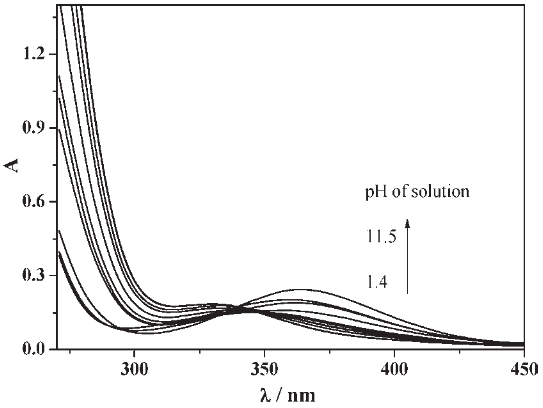

Figure 2. Experimental UV spectra of Pd^{2+}−NTA complex species recorded in aqueous solutions containing: $C_{Pd} = 4.5 \cdot 10^{-4}$ mol·kg^{-1}, $C_{NTA} = 1.6 \cdot 10^{-3}$ mol·kg^{-1}, I = 0.1 mol·kg^{-1} in $NaClO_4$, at T = 298.15 K.

As pointed out before, the stability constant of the PdL species (L = APC) is too high to be determined by classical potentiometric ISE-H^+ measurements carried out in noninteracting ionic media, such as $NaNO_3$ or $NaClO_4$. To overcome this difficulty, we followed a different approach based on potentiometric measurements in mixed interacting and noninteracting ionic media and on spectrophotometric measurements. First of all, an accurate check of literature data was made selecting, when possible, the most reliable values of the log $K_{Pd(APC)}$ for each system investigated.

These values were used, in the first approximation, to perform calculations on the experimental potentiometric data obtained from titrations of Pd^{2+}−APC solutions (APCs = NTA, EDTA, S, S-EDDS, DTPA, and TTHA) in $NaNO_3$ noninteracting ionic medium. In particular the following formation constant values from the literature data were used: log K_{PdNTA} = 17.1, log K_{PdEDTA} = 26.4, and log K_{PdDTPA} = 29.7.[28,29] In the case of S, S-EDDS and TTHA ligands, the log $K_{Pd(APC)}$ values of 13.6 and 18.73 (the only data present in literature) reported by Sunar et al. and by Napoli, respectively,[24,25] were considered too low and not consistent with those of the other Pd^{2+}−complexone systems. For this reason we decided to use for S,S-EDDS the same formation constant as for EDTA and for TTHA, the log $K_{Pd(TTHA)}$ = 37.2. The log $K_{Pd(TTHA)}$ value was obtained by using the empirical eq 4 for the dependence of Pd^{2+}−APC formation constants (APC = NTA, EDTA, DTPA, IDA)[29] on the number of amino (n_N) and carboxylic (n_{COOH}) groups and on their distance (expressed as the number of −CH− between these groups, d) in the APC ligand molecule:

$$\log K_{Pd(APC)}(\pm 0.6) = p_1 + p_2 n_N{}^2 + p_3 n_{COO} + p_4 d \tag{4}$$

where $K_{Pd(APC)}$ is the stability constant of the Pd^{2+}−APC species and p_1, p_2, p_3, and p_4 are empirical parameters. From the stability data used for the Pd(APC) species in the different systems considered we found: p_1 = 12.8, p_2 = 0.8, p_3 = 1.7, and p_4 = −0.7. By using these values for the Pd−TTHA system (n_N = 4, n_{COOH} = 6, and d = 1), the value of log K_{PdTTHA} = 37.2 was calculated.

These stability data for all of the Pd(APC) species in the different Pd^{2+}−APC systems were considered as a baseline for

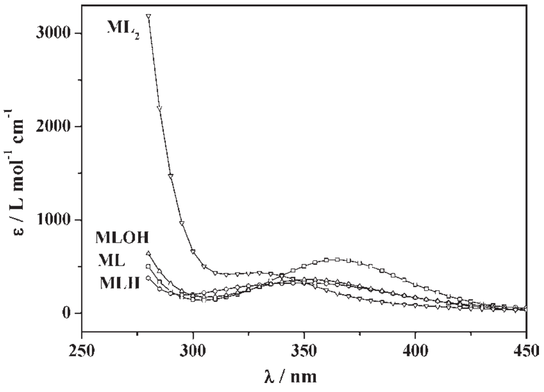

Figure 3. Molar extinction coefficients, ε ($L \cdot mol^{-1} \cdot cm^{-1}$), of Pd^{2+}—NTA complex species at $T = 298.15$ K.

the next two steps of our investigation in which ISE-H^+ potentiometric titrations in $NaClO_4$/NaI mixed ionic medium and spectrophotometric/ISE-H^+ potentiometric titrations in $NaClO_4$ ionic medium were carried out at $I = 0.1\ mol \cdot kg^{-1}$. By both potentiometric and spectrophotometric/potentiometric measurements, it was possible to calculate the log $K_{Pd(APC)}$ values and to validate the accuracy of the log β values of the Pd^{2+}—APC differently protonated or hydroxo species for all of the complexones considered. In fact, as results from potentiometric measurements carried out in $NaClO_4$/NaI mixed ionic medium, the iodide ion forms a very stable complex species with the palladium(II) ion ($\log K_{PdI} = 6.08$, $\log \beta_{PdI_2} = 22$, $\log \beta_{PdI_3} = 25.8$, $\log \beta_{PdI_4} = 28.3$ in $NaClO_4$/NaI, at $I = 1\ mol \cdot L^{-1}$);[46] the formation of the Pd^{2+}—I species leads to a reliable lowering of the formation percentage of Pd^{2+}—APC species and allows the calculation of the formation constants of ML species in all of the Pd^{2+}—APC systems. The reliability of complexation models of Pd^{2+}—APC systems obtained by ISE-H^+ potentiometry was confirmed by spectrophotometric titrations. In fact, all of the species, including the protonated and the hydroxo ones, formed in the Pd^{2+}—APC systems show intense bands in the wavelength range (250 to 400) nm. As an example, the UV spectra of the Pd^{2+}—NTA complex species in the pH range 1.4 to 11.64 and the molar extinction coefficients, ε_{max}, in the wavelength range (250 to 500) nm are reported in Figures 2 and 3.

Spectrophotometric investigations have been performed considering the following points: (i) the complexones (differently protonated) do not absorb in the spectral range investigated, (ii) the Pd^{2+} ion and its hydrolytic species normally absorb at these wavelengths (for $Pd(H_2O)_4{}^{2+}$ $\lambda_{max} = 379$ nm, $\varepsilon_{max} = 78\ L \cdot mol^{-1} \cdot cm^{-1}$),[47] (iii) in the pH range considered only the absorption of Pd^{2+}—APC species results, while the absorption of both the Pd^{2+} aquo ion and the palladium hydrolytic species is completely suppressed; (iv) as a consequence, in the data processing by Hypspec computer program,[40] the aquo ion and hydrolysis species of palladium(II) were not included in the list of absorbing species identified by factor analysis. Table 5 collects the maximum values of molar extinction coefficients, ε_{max} ($L \cdot mol^{-1} \cdot cm^{-1}$) of the Pd^{2+}—APC species and the corresponding wavelengths, λ_{max} (nm), obtained by the deconvolution of spectra determined in solutions containing different Pd^{2+}—APC concentration ratios, as reported in Table 2.

Finally, the potentiometric titration data in $NaNO_3$ ionic medium were reanalyzed by keeping constant the values of log $K_{(ML)}$ in the complexation models for all of the Pd^{2+}—APC systems. The results obtained by following this approach are reported in Table 6 together with the formation constants of all of the species obtained by potentiometry and spectrophotometry in the different ionic media.

Table 5. Spectroscopic Data for Pd^{2+}—APC Complex Species

	λ_{max}	ε_{max}
species	nm	$L \cdot mol^{-1} \cdot cm^{-1}$
	TTHA	
$Pd(TTHA)H_3$	325	976 ± 5
$Pd(TTHA)H_2$	325	1210 ± 6
Pd(TTHA)H	325	1330 ± 4
Pd(TTHA)	330	1080 ± 5
Pd(TTHA)(OH)	330	1070 ± 4
	DTPA	
$Pd(DTPA)H_3$	325	1010 ± 35
$Pd(DTPA)H_2$	325	1130 ± 29
Pd(DTPA)H	325	1390 ± 26
Pd(DTPA)	325	1410 ± 12
Pd(DTPA)(OH)	325	1330 ± 30
	EDTA	
$Pd(EDTA)H_2$	345	642 ± 6
Pd(EDTA)H	335	1040 ± 6
Pd(EDTA)	335	1270 ± 4
Pd(EDTA)(OH)	360	640 ± 13
	S,S-EDDS	
$Pd(S,S\text{-}EDDS)H_2$	325	1070 ± 12
Pd(S,S-EDDS)H	330	1200 ± 10
Pd(S,S-EDDS)	330	1310 ± 10
Pd(S,S-EDDS)(OH)	330	1350 ± 26
	NTA	
Pd(NTA)H	345	323 ± 5
Pd(NTA)	370	564 ± 4
Pd(NTA)(OH)	355	361 ± 8
$Pd(NTA)_2$	330	433 ± 7

As can be seen, simple PdL species, mononuclear protonated species, $PdL_qH_r{}^{(2-zq+r)}$ (the r value depends on the APC considered), and mixed hydroxo species, PdL(OH), are formed in all the systems investigated. Moreover, in the Pd^{2+}—NTA system the $Pd(NTA)_2$ species is formed too.

In general, APCs form very stable species with Pd^{2+} ion in the entire pH range (2 to 11.5) investigated, including the acidic pH range. For this reason, in spite of the high stability of hydrolytic species of palladium(II), which begin to be formed at low pH values (~2), the formation of simple hydrolytic species of the metal ion in the presence of APC ligands is suppressed in the whole pH range (2 to 11.5) investigated, as shown in the distribution diagrams reported in Figure 4 ($C_{Pd} = 1\ mmol \cdot kg^{-1}$, $C_{APC} = 2\ mmol \cdot kg^{-1}$, in Na^+ medium, at $I = 0.1\ mol \cdot kg^{-1}$ and at $T = 298.15$ K).

The stability of the Pd(APC) species follows the trend: TTHA > DTPA > EDTA > S,S-EDDS > NTA. As expected, the stability is a function of the number of binding groups (—NH and —COOH) present in the complexone molecule. In the case of S,S-EDDS and EDTA, which are structural isomers having the same number

Table 6. Formation Constants of Pd^{2+}−APC (NTA, S,S-EDDS, EDTA, DTPA, and TTHA) Complex Species Obtained with Different Techniques, at $I = 0.1\ \text{mol}\cdot\text{kg}^{-1}$ and at $T = 298.15$ K

species	$\log \beta_{pqr}$ [a,b]		
	potentiometry (ISE-H^+)		spectroscopy
ionic medium	$NaNO_3$	$NaClO_4$/NaI	$NaClO_4$
L = NTA			
PdLH	20.25 ± 0.01[c] (2.44)		20.00 ± 0.01[c] (2.19)
PdL	17.82		17.82 ± 0.01
PdL_2	24.50 (6.69) [d]		24.50 ± 0.01 (6.69) [d]
PdLOH	9.99 ± 0.02 (−7.83)		10.41 ± 0.01 (−7.41)
L = EDTA			
$PdLH_2$	28.3 ± 0.1 (1.57)	28.55 (2.01)	28.55 ± 0.01 (2.01)
PdLH	26.72 ± 0.01 (3.15)	26.54 (2.94)	26.54 ± 0.01 (2.97)
PdL	23.58	23.61 ± 0.09	23.58 ± 0.01
PdLOH	13.33 ± 0.01 (−10.25)	13.67 ± 0.07 (−9.94)	13.67 (−9.91)
L = S,S-EDDS			
$PdLH_2$	28.62 ± 0.01 (1.89)	28.62 (1.89)	28.62 (1.89)
PdLH	26.73 ± 0.01 (3.64)	26.73 (3.64)	26.73 (3.7)
PdL	23.1	23.1 ± 0.1	23.04 ± 0.01
PdLOH	12.00 ± 0.01 (−11.1)	12.00 (−11.1)	12.00 (−11.04)
L = DTPA			
$PdLH_3$	45.42 ± 0.01 (2.69)	45.42 (2.69)	45.42 (1.74)
$PdLH_2$	42.73 ± 0.02 (2.7)	42.73 (2.7)	43.68 ± 0.02 (2.9)
PdLH	40.03 ± 0.01 (3.66)	40.03 (3.79)	40.78 ± 0.03 (4.41)
PdL	36.38	36.25 ± 0.02	36.38 ± 0.04
PdLOH	24.95 ± 0.02 (−11.43)	24.87 ± 0.07 (−11.38)	24.3 ± 0.1 (−12.08)
L = TTHA			
$PdLH_3$	50.0 ± 0.1 (2.35)	50.0 (2.35)	50.0 (2.35)
$PdLH_2$	47.64 ± 0.03 (3.66)	47.64 (3.72)	47.64 (3.66)
PdLH	43.98 ± 0.01 (6.87)	43.92 ± 0.03 (7.05)	43.98 (6.87)
PdL	37.12	36.88 ± 0.05	37.12 ± 0.01
PdLOH	27.34 ± 0.02 (−9.78)	26.59 ± 0.02 (−10.29)	27.34 (−9.74)

[a] $\log \beta_{pqr}$ refers to eq 1 and are expressed in molal ($\text{mol}\cdot\text{kg}^{-1}$) concentration scale; $L^{z-} = NTA^{3-}$, S,S-$EDDS^{4-}$, $EDTA^{4-}$, $DTPA^{5-}$, or $TTHA^{6-}$; negative r values stand for OH^-. [b] Stepwise formation constants $\log K_{pqr}$ in parentheses refer to eq 2 or in the case of the PdL(OH) species to $PdL^{(z-2)-} + OH^- = PdL(OH)^{(z-1)-}$. [c] ± Standard deviation. [d] Stepwise formation constants in parentheses refer to the reaction: $Pd(NTA)^- + NTA^{3-} = Pd(NTA)_2{}^{4-}$.

of amino and carboxylic binding groups, the following other factors must be considered in evaluating the relative stability of complex species: (i) the nature of amino groups, which are tertiary in the EDTA and secondary in S,S-EDDS, and (ii) the distance between binding groups in the molecule.

3.4. Sequestering Ability of APCs toward the Palladium(II) Ion and Other Divalent Metal Ions. The stability data obtained for all of the species in the different Pd^{2+}−APC systems were used to evaluate the sequestering capacity of the complexones under investigation toward the palladium(II) ion. Moreover, since the natural waters and wastewaters are multicomponent solutions where different metal ions can be present simultaneously, the sequestering capacity of the same ligands was also evaluated, for comparison, toward other metal ions (Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}) of environmental and biological interest. This investigation is useful to assess the sequestration capability of the complexones (i) in multicomponent solutions, such as natural waters and wastewaters, where different metal ions can be present simultaneously and can compete in metal complex formation with the ligands also present, (ii) in some industrial applications where the choice of the best sequestering agent to remove undesirable metal ions is often important, and (iii) in agricultural practices where complexones can be used as sequestering agents in the chelate-assisted metal phytoextraction.[18,48,49]

For the above reasons, it can be very useful to have a parameter able to give immediate information on the sequestering ability of a ligand (in our case APCs) toward metal ions in the conditions (ionic medium composition, ionic strength, pH, metal ion concentration, etc.) of the medium where the metal sequestration occurs (e.g., contaminated natural waters, wastewaters, or waters used in a particular industrial process). The sequestering ability of a generic ligand is, of course, strictly related to the stability of the complex species formed with the metal ion, but also to all of the possible competing reactions involving both the ligand and the metal ion, that is, on their speciation. Therefore, the knowledge of the stability of the metal−ligand complex

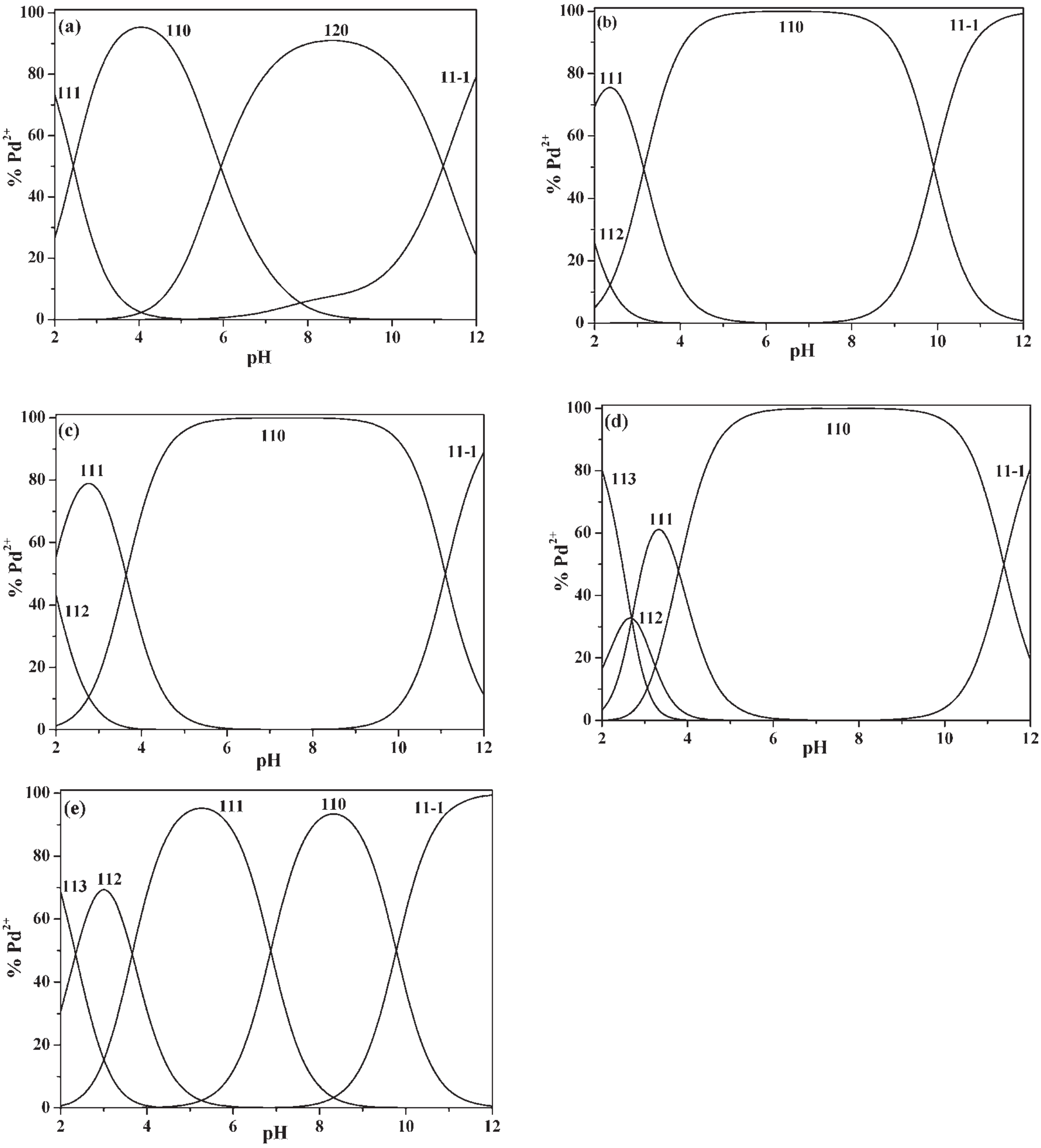

Figure 4. Distribution diagrams of $Pd_pLH_r^{(z-2p-r)-}$ species vs pH, at $I = 0.1\ \text{mol}\cdot\text{kg}^{-1}$ in $NaNO_3$, at $T = 298.15$ K; $L^{z-} = NTA^{3-}$ (a), S,S-$EDDS^{4-}$ (b), $EDTA^{4-}$ (c), $DTPA^{5-}$ (d), and $TTHA^{6-}$ (e). Experimental conditions: $C_{Pd} = 1\ \text{mmol}\cdot\text{kg}^{-1}$, $C_L = 2\ \text{mmol}\cdot\text{kg}^{-1}$. p1r indexes in figures refer to $Pd_pLH_r^{(z-2p-r)-}$ species, and negative r values stand for OH^-.

species only is not sufficient to assess the efficiency of a sequestration process, but the speciation picture of both the metal and the ligand must be also known. An objective representation and quantification of the sequestering ability of a ligand toward a metal ion can be given by the semiempirical parameter pL_{50} that represents the total ligand concentration necessary to bind (sequestrate) the 50% of trace metal ion present into the solution. This parameter, already successfully tested for various systems (see, e.g., refs 30−33), is obtained by the following Boltzmann-type equation:

$$\sum\% = \frac{A_1 - A_2}{1 + e^{(pL - pL_{50})/S}} + A_2 \tag{5}$$

where Σ% represents the total percentage of metal complex species (Pd^{2+} or the other divalent metal ions, in our case) formed with the ligand considered, $A_1 = 100$ (Σ% for pL → 0) and $A_2 = 0$ (Σ% for pL → ∝), and S is the curve slope at 50 % complexation, which is always equal to 0.434. In the light of these considerations, eq 5 can be written as:

$$\sum\% = \frac{100}{1 + 10^{(pL - pL_{50})}} \tag{5a}$$

More details about the pL_{50} calculation and the method used to draw the sequestration diagrams can be found in ref 33, where a comparison between pL_{50} and similar parameters is also given. Briefly, the sequestration diagrams are drawn by plotting in the y-axis the sum of all of the metal(II) complex species with the ligand (APC, in our case) calculated considering different ligand concentrations and $C_{M^{2+}} = 10^{-14}\ \text{mol}\cdot\text{kg}^{-1}$. In this way, the pL_{50}

Table 7. Values of pL_{50} for the Sequestration of Pd^{2+} and Other Divalent Metal Ions[a] by NTA, S,S-EDDS, EDTA, DTPA, and TTHA, at pH = 6, in $NaNO_3$ Ionic Medium, at I = 0.1 $mol \cdot kg^{-1}$ and T = 298.15 K

	pL_{50}				
metal ion	NTA	S,S-EDDS	EDTA	DTPA	TTHA
Pd^{2+}	10.75	13.90	16.01	25.87	25.89
Cu^{2+}	9.36	13.30	14.96	14.71	15.80
Pb^{2+}	8.14	7.77	13.99	12.15	12.26
Zn^{2+}	7.32	8.66	12.49	11.87	12.17
Cd^{2+}	6.43	5.17	12.50	12.46	13.52
Hg^{2+}	5.47	7.11	12.00	14.35	14.93
Ca^{2+}	2.97	0.70	6.83	4.41	5.00
Mg^{2+}	2.16	1.30	4.98	3.53	4.32

[a] The stability constants of hydrolytic species are from ref 50; complex formation constants of M^{2+}−APC species are from ref 12.

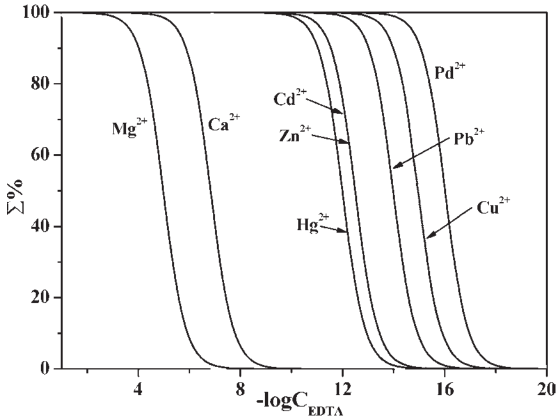

Figure 5. Total percentage of M^{2+} ions complexed (Σ%) by EDTA vs $-\log C_{EDTA}$ and at T = 298.15 K. Experimental conditions: $C_{M^{2+}} = 10^{-14}$ $mol \cdot kg^{-1}$ (trace), pH = 6, I = 0.1 $mol \cdot kg^{-1}$ in $NaNO_{3aq}$.

varies with the experimental conditions (pH, ionic strength, supporting electrolyte, temperature, etc.), but it is independent of the analytical concentration of the metal ion. Moreover, since all of the side interactions occurring in the system (metal hydrolysis, ligand protonation, interactions with other components) are taken into account in the speciation model, they are not considered in the calculation of pL_{50} since they do not contribute to the pL_{50} parameter as previously defined. On the basis of these considerations it can be concluded that the stronger the binding ability of the ligand, the higher the pL_{50} is. Table 7 shows the pL_{50} values calculated for the sequestration of Pd^{2+} and the selected other divalent metal ions by the APCs at pH = 6, at I = 0.1 $mol \cdot kg^{-1}$ and at T = 298.15 K. With the exception of the pL_{50} values of Pd^{2+}−APC systems, the sequestration parameters of the complexones toward the other M^{2+} ions were calculated by using hydrolysis and complex formation constants taken from the literature.[12,50]

Figure 5 shows, as an example, the sequestration curves of EDTA toward all divalent metal ions considered, at pH = 6.0. At this pH the sequestration capability of EDTA toward Pd^{2+} ion is higher than the one toward the other divalent metal ions.

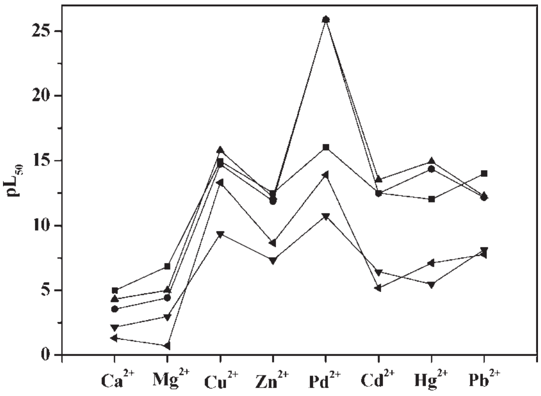

Figure 6. pL_{50} values for divalent metal ions sequestration by APCs (NTA, S,S-EDDS, EDTA, DTPA, and TTHA). Experimental conditions: $C_{M^{2+}} = 10^{-14}$ $mol \cdot kg^{-1}$ (trace), pH = 6, in Na^+ ionic medium, at I = 0.1 $mol \cdot kg^{-1}$ and at T = 298.15 K. Symbols: ■, EDTA; ●, DTPA; ▲, TTHA; ▼, NTA; ◀, S,S-EDDS.

The same behavior is shown by all APCs considered here, as can be seen in Figure 6 where the pL_{50} values (see Table 7) of NTA, S,S-EDDS, EDTA, DTPA, and TTHA are plotted for all divalent metal ions considered at the same pH and metal concentration conditions.

As pointed out before, the sequestering capacity of a ligand toward a metal ion is strictly dependent on the pH of the medium where the metal sequestration occurs. Figure 7a−e shows the dependence on pH (in the range 2 to 10) of pL_{50} for each APC ligand used toward the metal ions considered.

By using the pL_{50} data, empirical relationships can be found for the dependence on pH. In particular, the dependence on pH of pL_{50} of APC ligands toward Pd^{2+} ion can be expressed by the following equation:

$$pL_{50} = p_1 + p_2(\mathrm{pH} - p_3)^2 \qquad (6)$$

where p_1, p_2, and p_3 are empirical parameters whose values are reported in Table 8.

3.5. Literature Comparison. Among synthetic chelating agents the APCs are the most used and, as a consequence, the most studied in terms of their sequestration capability toward metal ions.[12] Analogously, palladium(II), as the other PGE, is the object of the research of many scientists that deal with speciation study in natural systems. Despite the great environmental importance of both APC ligands and palladium(II) ion, in literature there are relatively few and dated papers[24−29] dealing with the determination of complexation ability of the former toward the latter. The lack of thermodynamic data on palladium(II)−APC complexes is probably due to (i) the difficulty in the calculation of hydrolysis constants of palladium(II) ion, that in $NaNO_3$ ionic medium undergoes hydrolysis at pH < 2 and (ii) the high stability constant values of the APCs complex species.

All of the literature data on Pd^{2+}−complexones interactions are reported in Table 1. From their critical analysis emerges that some of these data (e.g., stability constants of Pd^{2+}−TTHA complex species reported by Napoli,[25] the log $K_{Pd(S,S\text{-}EDDS)}$ reported by Sunar et al.[24] and the log $K_{Pd(EDTA)}$ reported by MacNevin and Kriege[26]) do not meet criteria for their selection by the most important database for stability constants such as, for example, the NIST database. Moreover, most of the other literature stability constants of Table 1 are classified by NIST as "tentative" or "provisional" data,[12] with the exception of log $K_{Pd(DTPA)}$ = 29.7, log $K_{Pd(DTPA)H}$ = 3.50,

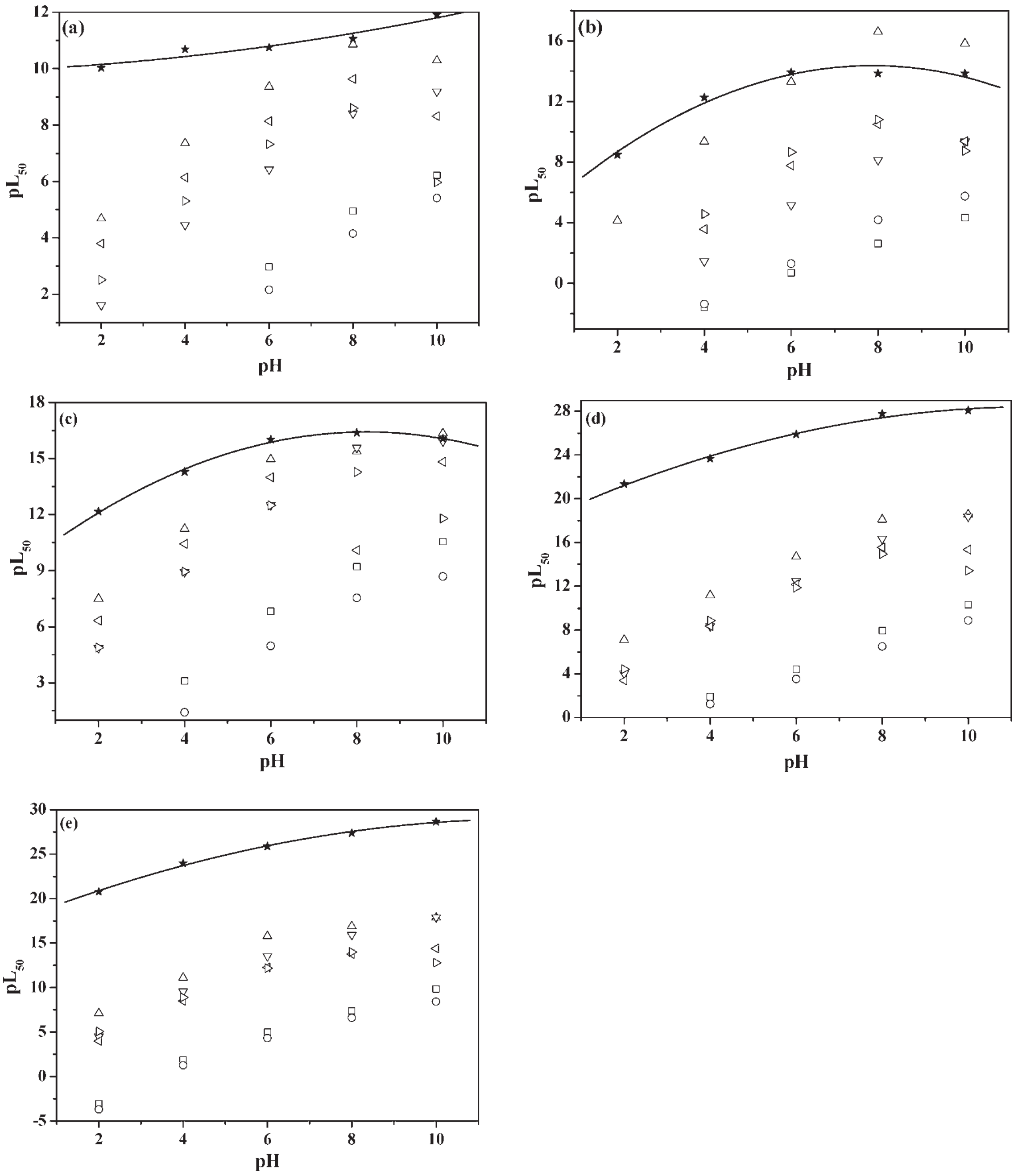

Figure 7. Dependence on pH of pL_{50} of NTA (a) S,S-EDDS (b), EDTA (c), DTPA (d), and TTHA (e) toward the divalent metal ions. Experimental conditions: Na^+ ionic medium, $I = 0.1$ mol·kg^{-1} and $T = 298.15$ K. Symbols: □, Ca^{2+}; ○, Mg^{2+}; △, Cu^{2+}; ▽, Cd^{2+}; ◁, Pb^{2+}; ▷, Zn^{2+}; ★, Pd^{2+}.

Table 8. Parameters of Equation 6 for the Dependence on pH of pL_{50} of APCs towards the Pd^{2+} Ion

APC	p_1	p_2	p_3	σ^a
NTA	10.14	0.02	0	0.22
EDTA	16.40	−0.1	8.23	0.15
S,S-EDDS	14.5	−0.17	7.9	0.50
DTPA	28.4	−0.07	11.8	0.33
TTHA	29.1	−0.07	12.7	0.24

[a] Standard deviation on the fit.

and $\log K_{Pd(EDTA)} = 24.5$ reported by Anderegg and Malik[29] that are labeled as "recommended" stability constants.[12]

The different experimental conditions (ionic medium, ionic strength, temperature) together with the low reliability of a consistent part of literature stability constants make the comparison with our thermodynamic data very difficult.

However, by taking into account the different experimental conditions used by the different authors, the following considerations can be made.

(i) There is a good agreement between our and literature values of $\log K_{11r}$. For example, our $\log K_{111}$ values for the Pd^{2+}–TTHA, Pd^{2+}–DTPA, Pd^{2+}–EDTA, and Pd^{2+}–NTA systems are: 6.96, 3.96, 3.06, and 2.31, respectively [$I = 0.1$ mol·kg^{-1} (Na^+ medium), $T = 298.15$ K]. The analogous $\log K_{111}$ of literature are: 6.92 [$I = 0.5$ mol·L^{-1}

Table 9. Suggested $\log \beta_{pqr}$ Values[a] of Pd^{2+}−L Species (L = NTA, S,S-EDDS, EDTA, DTPA, and TTHA) in Na^+ Ionic Media, at I = 0.1 mol·kg^{-1} and T = 298.15 K

species	$\log \beta_{pqr}$				
L	TTHA	DTPA	EDTA	S,S-EDDS	NTA
PdL	37.0 ± 0.1	36.31 ± 0.07	23.60 ± 0.01	23.07 ± 0.03	17.82 ± 0.01
PdLH	43.95 ± 0.03	40.4 ± 0.4	26.63 ± 0.09	26.73 ± 0.01	20.1 ± 0.1
$PdLH_2$	47.64 ± 0.03	43.2 ± 0.5	28.4 ± 0.1	28.62 ± 0.01	
$PdLH_3$	50.0 ± 0.1	45.42 ± 0.01			
PdLOH	27.0 ± 0.4	24.7 ± 0.3	13.5 ± 0.2	12.00 ± 0.01	10.2 ± 0.2
PdL_2					24.50 ± 0.01

[a] $\log \beta_{pqr}$ refers to eq 1 and are expressed in molal (mol·kg^{-1}) concentration scale.

($NaClO_4$), T = 298.15 K],[25] 3.50 [I = 1 (0.2 + 0.8) mol·L^{-1} ($NaBr/NaClO_4$ mixed medium), T = 293.15 K],[29] 3.01 [I = 1 mol·L^{-1} ($NaClO_4$), T = 293.15 K],[29] and 2.48 [I = 1 mol·L^{-1} ($NaClO_4$), T = 293.15 K).[29]

(ii) A rough comparison can be made between the value of $\log \beta_{PdEDTA}$ = 23.60 [I = 0.1 mol·kg^{-1} (Na^+ medium), T = 298.15 K] reported here and the values for the same species reported by Anderegg et al.[29] [$\log \beta_{PdEDTA}$ = 24.5 at I = 1 mol·L^{-1} ($NaClO_4$), T = 293.15 K) and by Kragten et al. [$\log \beta_{PdEDTA}$ = 26.4 at I = 0.1 mol·L^{-1} (medium not reported), T = 293.15 K,[28] and $\log \beta_{PdEDTA}$ = 25.6 at I = 0.2 mol·L^{-1} ($NaClO_4$), T = 294.15 K[27]].

(iii) Also the $\log \beta_{PdNTA}$ = 17.82 [I = 0.1 mol·kg^{-1} (Na^+ medium), T = 298.15 K] obtained here is comparable with the stability constant reported by Anderegg et al. ($\log \beta_{PdNTA}$ = 17.1 at I = 0.1 mol·L^{-1} ($NaClO_4$), T = 293.15 K].[29]

4. CONCLUSIONS

A systematic study on the binding capacity of five complexones toward Pd^{2+} ion in Na^+ ionic media was made by potentiometric and spectroscopic techniques. Hydrolysis constants of metal ions, protonation constants of APC, and, in the case of measurements in $NaClO_4$ /NaI ionic medium, formation constants of PdI_n species were all considered in the speciation model of Pd^{2+}−APC systems. The stability of the Pd(APC) species follows the trend: TTHA > DTPA > EDTA > S,S-EDDS > NTA, and as expected, the stability is a function of the number of binding groups (−NH and −COOH) present in the APC molecule, but this trend is not linear. If we consider the homogeneous series, NTA, EDTA, DTPA, and TTHA, with the general formula $N_n(CH_2)_{3n}(COOH)_{n+2}$ the following sigmoidal equation can be written for $\log \beta_{PdL}$ as a function of n:

$$\log \beta = a\left[\frac{1-b}{1+10^{(n-b)}} + b\right] \tag{7}$$

with a = 16.73 and b = 2.28. The parameter a refers to the theoretical minimum $\log \beta$ value (for $n \rightarrow 0$) and b is the n value corresponding to the maximum slope for the function $\log \beta$ versus n. A similar behavior can be found for $\log \beta_{CuL}$ [I = 0.1 (K^+) mol·L^{-1}],[12] with a = 12.19 and b = 1.79.

The suggested formation constants of Pd^{2+}−APC complex species at I = 0.1 mol·kg^{-1}, in Na^+ ionic medium, at T = 298.15 K are reported in Table 9.

The stability data calculated for the Pd^{2+}−APC complex species were used to quantitatively define, in terms of pL_{50}, the sequestration capability of APCs toward the palladium(II) ion. Some considerations can be done on the basis of pL_{50} values: (i) all of the APCs considered strongly sequestrate Pd^{2+} in the pH range investigated; (ii) a comparison of pL_{50} of the complexones for different divalent metal ions (Ca^{2+}, Mg^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}) evidenced that in the pH range typical of natural fluids (6 to 8) all of the APCs preferentially sequestrate the palladium(II) ion; (iii) although among the APCs considered the S,S-EDDS is not the best sequestering agent for Pd^{2+} ion, its high biodegradability and a sufficient high pL_{50} in the pH range investigated make this APC the best choice when it is necessary to conjugate an environmental friendly and a good sequestration treatment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Protonation constants for the series (Table 1S), iodo complex species in mixed medium (Table 2S), formation constants of the complex series (Table 3S), and suggested $\log \beta_{pqr}$ values (Table 4S). This material is available free of charge via the Internet at http://pubs.acs.org.

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