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Speciation of iridium(IV) in hydrochloric acid medium by means of capillary zone electrophoresis and spectrophotometry

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Abstract

Speciation of iridium(IV) [Ir(IV)] in hydrochloric acid solutions at different proton concentrations (between 1 and 10^{-3} *M*) has been studied using capillary zone electrophoresis and spectrophotometry in order to determine the number of species that are formed during the aquation and hydrolysis of the hexachloro complex of Ir(IV). The formation of more than seven species was found. The presence of $[IrCl_6]^{2-}$, $[Ir(H_2O)Cl_5]^{-}$ and $[Ir(OH)Cl_5]^{2-}$ species of Ir(IV) and $[Ir(H_2O)Cl_5]^{2-}$ and $[Ir(OH)Cl_5]^{3-}$ of Ir(III) give the best explanation of the obtained results. The formation of other species detected in solution can be explained by the formation of dimers of the aquated species by the formation of hydroxo bridges. A spontaneous reduction of Ir(IV) to Ir(III) has been proved in all the solution studied. The extension of this process increases at higher pH values. Other peaks that appear in the electropherograms are associated to the formation of dimers of the aquated species by means of hydroxo bridges.

Keywords: Iridium; Metal complexes

1. Introduction

The knowledge of the binding state and binding partners of metal ions is important information about their behavior and their reactivity with other compounds. This knowledge is especially important for prediction of metal ions behavior in biological and physiological systems to estimate their toxicological and nutrition physiological relevance.

It is well known that platinum group metals (PGMs) (Pt, Pd, Rh, Ru, Ir and Os) form soluble chloro complexes in hydrochloric acid (HCl) solutions at different pH values, but they are easily hydrolyzed when the acidity decreases. This effect is not the same for all the PGMs. In some cases, chloro complexes can hydrolyze even in strongly acidic media; it is known that rhodium forms immediately the $[Rh(H_2O)Cl_5]^{2-}$ complex in concentrated HCl [1]. The behaviour of iridium (Ir) is very similar to rhodium, but the chemistry of the Ir–chloro complexes in aqueous solutions is still not well known.

Different species, like $[Ir(H_2O)_3Cl_3]^{+}$, $[Ir(H_2O)_2Cl_4]$, $[Ir(H_2O)Cl_5]^{-}$, $[Ir(OH)_2Cl_4]^{2-}$ and $[Ir(OH)_4Cl_2]^{2-}$, have been reported in solution at different pH [2]. Also, a fast exchange of Ir between $[IrCl_6]^{2-}$ and $[IrCl_6]^{3-}$ has been reported in dilute acid solution [2]. However, the speciation of Ir(IV) in HCl aqueous solutions is not known sufficiently.

One of the principal problems in determining the speciation of Ir–chloro complexes is the problem of applying suitable analytical methods and the difficulties in finding a separation method for the analysis of

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individual metal-containing species. This method should not impair the binding between the metal and the counter-ions.

UV–visible spectrophotometry has been used sometimes, but the results obtained only explain the formation of two complexes following the reaction (A),

$$IrCl_6^{2-} + H_2O \leftrightarrow Ir(H_2O)Cl_5^- + Cl^- \quad (A)$$

which indicates a possible second reaction of the aquation to form $Ir(H_2O)_2Cl_4$ [3].

HPLC has been used to separate and determine the PGMs. Using reversed [4–6] and normal-phase [7] chromatography, previous complexation of the metals with a chelating reagent is required and this does not allow us to find the different species present in solution for the same metal.

Ion chromatography has been used for the speciation of platinum–aquo–chloro complexes [8] and to separate and determine some PGMs [9] in HCl solutions. Ir has not been studied until now with this method.

In the last years, the applications of capillary zone electrophoresis (CZE) to determine inorganic compounds has increased [10], and recently, several studies about the determination of PGMs in acidic media using CZE [11–16] has been reported. This technique appears to be promising for its use in the speciation of the aquo–chloro complexes of the PGMs. For example, Thornton and Fritz [15] found that old solutions of Ir(IV) show different peaks in the electropherogram but the authors did not study the equilibria of the formation of these compounds.

The possibility of work at low pH values using a HCl buffer shows that CZE appears to be a suitable analytical method for the speciation study of Ir in HCl media. The condition is that the equilibria concerning Ir–chloro complexes are slow in comparison with the duration of the experiments (inert systems). This condition is fulfilled in this case.

In this paper, speciation of Ir(IV) in acidic chloride media at different proton concentrations (between 10^{-3} up to 1 *M*) is elucidated and described using CZE measurements. In addition to CZE, spectrophotometric measurement was used to follow spectral changes during aquation and hydrolysis reactions of Ir(IV) chloride.

2. Experimental

2.1. Apparatus

CZE was performed with a SpectraPhoresis 2000 (Thermo Bioanalysis, CA, USA). The unmodified fused-silica capillary used (Avery Denisson, MA, USA) was 75 cm×75 μm I.D.. The distance to the detector window was 62.5 cm. A reverse polarity of the CZE system (cathodic injection and anodic detection) was used. A voltage of −12 kV was applied, and the temperature was maintained constant at 25°C. Direct UV detection, typically at 210 nm, was used during the work and, in addition, scanning detection in the whole spectral range was used to obtain the spectra of the individual species separated.

Spectrophotometric measurements were done with a Hewlett-Packard 8453 diode-array spectrophotometer, using a 1-cm quartz cell.

2.2. Procedure

A new capillary column was conditioned by rinsing with 0.1 *M* NaOH for 1 h followed by a 1-h rinse with pure water. Prior to use, the capillary was each day washed for 10 min with 0.1 *M* NaOH, water for 10 min, 0.2 *M* HCl for 10 min, again with water for 10 min and the background electrolyte (BGE) solution for 30 min. Between runs the capillary was flushed with 0.2 *M* HCl for 2 min, followed by flushing with pure water for 2 min and the background electrolyte solution for 4 min. In this conditions the migration time values of the separated species were constant. At the end of daily work, the capillary was flushed with 0.2 *M* HCl for 1 min, water for 2 min, 0.1 *M* NaOH for 1 min and water for 5 min.

CZE measurements were done at a total Ir(IV) concentration of about 50 mg l^{-1}, while spectrophotometric measurements were done at higher concentrations (about 150 mg l^{-1}) in order to reach sufficient absorbance values.

2.3. Reagents

Ir(III) and Ir(IV) standard stocks solutions were prepared by weighing $(NH_4)_3IrCl_6 \cdot H_2O$ and $IrCl_4$

salts, respectively. Both salts were obtained from Johnson Mattey (Karlsruhe, Germany). The salts were dissolved in HCl at the working pH. Concentration of working solutions was checked by an inductively coupled plasma method, using an atomic absorption standard (Aldrich, Milwaukee, USA) of 1010 mg ml^{-1} to construct the calibration curve.

All other chemicals were of analytical grade purity and were obtained from Lachema (Brno, Czech Republic). Double-distilled water from a quartz still (Heraeus, Hanau, Germany) was used for the preparation of the solutions used in this study. Carrier electrolytes were prepared by mixing appropriate volumes of 1 *M* HCl, 1 *M* KCl and pure water. The BGE was prepared daily, filtered through a 0.45 μm filter prior to use and degassed in the ultrasonic bath for 10 min.

3. Results and discussion

3.1. Optimisation of the CZE conditions

In order to determine the best conditions for the CZE separation of the different complexes, the effect of the separation voltage, temperature and sample injection has been studied and optimised.

3.1.1. BGE selection

Previous spectrophotometric studies showed that the kinetic of the hydrolysis of Ir–chloro complexes is strongly dependent on the pH. This feature determines the selection of the electrolyte for the CZE. In previous works [13–16], a mixture of alkali metal chloride and HCl has been recommended as an appropriate electrolyte. Baraj et al. [13] used a BGE containing 0.4 *M* NaCl and 0.1 *M* HCl with a low applied voltage of −7 kV, but we have found that this electrolyte showed bad results for the determination of Ir, with migration times higher than 60 min. Thornton and Fritz [15] found that the electropherograms were very poor when the pH of the BGE was below 1.8. For this reason, we have used the value of pH equal to 2 for the electrolyte.

The concentration of total chloride in the BGE was maintained constant at 60 m*M* because this concentration was found optimal by Pirogov and Havel [16]. Following these conditions the BGE used was 50 m*M* KCl and 10 m*M* HCl.

3.1.1.1. Experimental procedure

Ir solutions with HCl concentration in the range 0.1–1 *M* were used, a portion of this working solution was then diluted to reach pH≈2 and this solution was immediately analysed by CZE.

3.1.2. Influence of the temperature

It is known that elevated temperature can shorten analysis time and in certain cases can improve the selectivity of the determination. We have found a decrease in the migration time of the species by increasing the temperature, but at same time a decrease in the efficiency of the measurements was observed (Table 1). This can be explained by a higher stability of the complexes at lower temperatures. For this reason, 25°C was chosen as the optimal temperature for the next work.

3.1.3. Influence of the separation voltage

The increase of the separation voltage produces a drift of the baseline, but decreased the time of the analysis (from 32 min for the first peak at −6 kV to

Table 1
Influence of the temperature during CZE separation on the determination of 8 ppm Ir(IV) (pH=1).

Temp. (°C)	Average current (μA)	Migration time (min)		Peak height (mAU)		Efficiency	
		1^{st} Peak	2^{nd} Peak	1^{st} Peak	2^{nd} Peak	1^{st} Peak	2^{nd} Peak
25	83.4	9.89	16.86	5660	782	95.97	85.02
30	88.3	9.34	15.87	6030	826	83.81	75.37
40	94.1	8.42	14.07	6690	928	62.55	61.29

BGE: 50 m*M* KCl and 10 m*M* HCl, detection at 210 nm.
Injection time: 10 s (hydrodynamic).
Separation voltage: −12 kV; mAU is absorbance in absorbance units $\times 10^3$.

8 min at −18 kV). For separation voltages higher than −10 kV a strong reduction of the separation efficiency of the Ir determination was observed. At voltages lower than −12 kV the efficiency of the determination was practically constant and little changes in the migration time have been observed. On the other hand, the drift of the baseline was found to be important at voltages lower than −12 kV. The voltage of −12 kV was chosen as the optimal one.

3.1.4. Influence of the sample injection time

Hydrodynamic injection was selected for all the experiments in this work. The increase of the injection time of the sample increases the sensitivity of the determination, but it produces a decrease in the efficiency as can be observed in Table 2 and increases the migration time. In these conditions, an injection time of 7 s was chosen as the optimal one.

3.2. CZE measurements

First of all, an attempt was made to calculate the electroosmotic flow (EOF) for the experimental conditions selected. As had been expected the EOF value at low pH is low [13,15], and thus no peak for a neutral compound (mesityl oxide) was obtained even after 2 h. This indicates that all the peaks observed correspond to the formation of anionic compounds in the solution. The possible presence of species with low mobility, and neutral or cationic species, was followed by a postwash with BGE during 2 min, but, in these conditions, no more peaks were obtained in all the solutions studied in this work.

Fig. 1 shows the electropherograms obtained at pH 3 (Fig. 1a) and 1 (Fig. 1b). The evolution of the different peaks with time can be observed from these figures. Previous work [15] indicates the presence of only four species in Ir(IV) solutions, and two of them were suggested to be due to Ir(III) compounds. However, as follows from Fig. 1, a higher number of peaks was observed, which indicates the presence of more species in solution. In order to elucidate and/or determine the presence of chloro complexes of Ir(III), two different experiments were done. Titrations [17] of some old solutions were done in order to determine if all the Ir in these solutions was Ir(IV) or if there was the presence of Ir(III) compounds. After the titrations demonstrated the reduction of a part of the Ir(IV) to Ir(III), electropherograms of Ir(III) solutions in HCl were done in order to determine which of the peaks are due to the Ir(III)–chloro complexes.

Mobility of the species depends first of all on the overall charge, the lower the charge, the slower is species migration and thus the higher is the migration time. The electropherograms obtained for the different pH values can be explained assuming the formation of $IrCl_6^{2-}$ species (migration time of 8.5 min), $[Ir(H_2O)Cl_5]^-$ (21.5 min) and $[Ir(OH)Cl_5]^{2-}$ (13.7 min) corresponding to Ir(IV) and $[Ir(H_2O)Cl_5]^{2-}$ (11.2 min) and $[Ir(OH)Cl_5]^{3-}$ (8.1 min) corresponding to Ir(III). As for the other peaks we suggest the formation of dimers from the aquated complexes by hydroxo bridges, but the percentage of

Table 2
Influence of injection time on separation patterns of Ir(IV) at the concentration of 8 mg l^{-1} Ir(IV) (pH=1)

Injection time (s)	Peak height (mAU)		Efficiency	
	1st Peak	2nd Peak	1st Peak	2nd Peak
2	620	973	233.7	150.0
4	1020	1770	175.9	121.9
7	1470	2860	115.4	86.2
10	1560	3620	63.9	61.6
20	1780	4560	13.3	24.3

BGE: 50 m*M* KCl and 10 m*M* HCl, detection at 210 nm.
Temperature: 25°C.
Separation voltage: −12 kV.

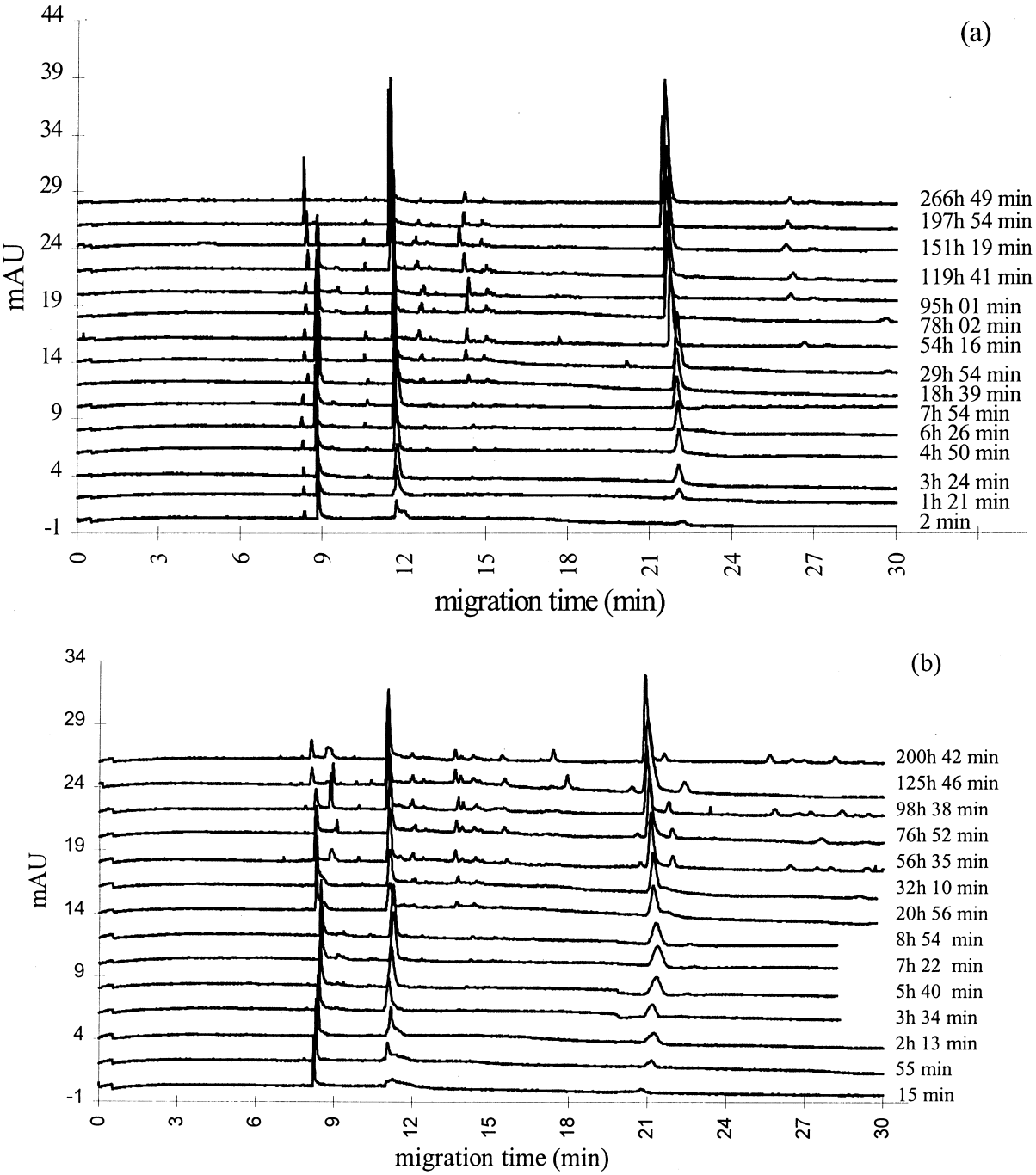

Fig. 1. Electropherograms patterns at pH 3 (a) and 1 (b) as a function of time. Conditions: BGE, 50 m*M* KCl and 10 m*M* HCl, pH = 1.98; temperature, 25°C; injection, hydrodynamic for 7 s.

these compounds are lower with respect to formation of the other compounds indicated above.

In all the solutions studied, the first peak appears at migration time equal to 8.5 min ($[Ir^{IV}Cl_6]^{2-}$), and the results indicate that it is less stable at higher pH values, where it disappears after about 200 h at pH = 3 and after 400 h at pH = 2.

Sometimes, a broad peak with the migration time corresponding approximately to 15 min was observed (Fig. 2) in the first of 6–7 h of kinetic study, but its reproducibility was very poor. After many experiments, we can conclude that the formation of this compound is hardly dependent on the method of solution preparation, and it appears always when the solid salt of Ir(IV) was dissolved in 1 *M* HCl and just only manual shaking was applied and the solution was diluted with water to the working pH value. This peak was eliminated when starting solution was placed in the ultrasonic bath for about 15 min before to analysis. This observation and the shape of the peak formed seem to indicate the formation of an higher associate, probably a dimer, previous to the formation of the hexachloroiridium(IV). The studies in solutions with acidity equal to 1 *M* indicate that the second species formed corresponds to the peak with migration time 21.5 min ($[Ir(H_2O)Cl_5]^-$). At other pH values, this peak is formed practically at the same time that the species with migration time 11.2 min ($[Ir(H_2O)Cl_5]^{2-}$). It indicates that the reduction of Ir(IV) to Ir(III), which occurs at all the pH values studied, is faster when increasing the pH.

Species $[Ir(H_2O)Cl_5]^-$ and $[Ir(H_2O)Cl_5]^{2-}$ are predominant at all pH values studied, with a higher abundance of the first one, corresponding to Ir(IV). This species can be seen during the first hours in all the cases and for its formation and transfer to Ir(III) compound we suggest the reaction scheme (B):

$$[IrCl_6]^{2-} \rightarrow [Ir(H_2O)Cl_5]^- \leftrightarrow [Ir(H_2O)Cl_5]^{2-} \qquad (B)$$

Fig. 3 shows the evolution of the ''peak area'' for these two species with time. It is possible to observe that the evolution of the two species is very similar for all pH values studied, with higher values for the species corresponding to the migration time 21.5 min.

During the experimental conditions selected, no equilibrium state of the solution was accomplished. It indicates that, probably, the aquation of the Ir–chloro complexes continue until the formation of other different aquated species, depending on the pH of the solution.

The other observed peaks can be explained by the hydrolysis reaction and thus possible formation of $Ir^{IV}Cl_5OH^{2-}$ (13.7 min) and $Ir^{III}Cl_5OH^{3-}$ (8.1 min). This assumption is supported by the fact that these peaks do not appear at proton concentrations equal to 1 *M*, and they only appear at pH 1 (only the first peak indicated), also at pH 2 and 3, with a higher

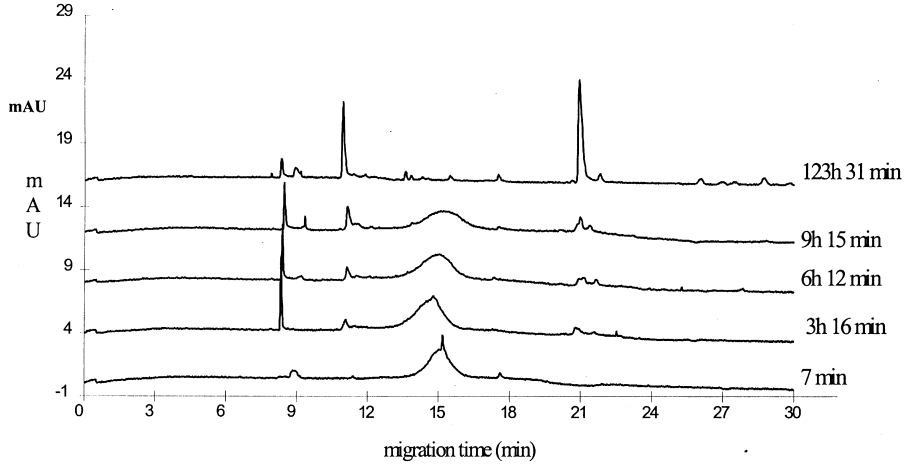

Fig. 2. Electropherogram obtained at pH 1 for a solution prepared without treatment.

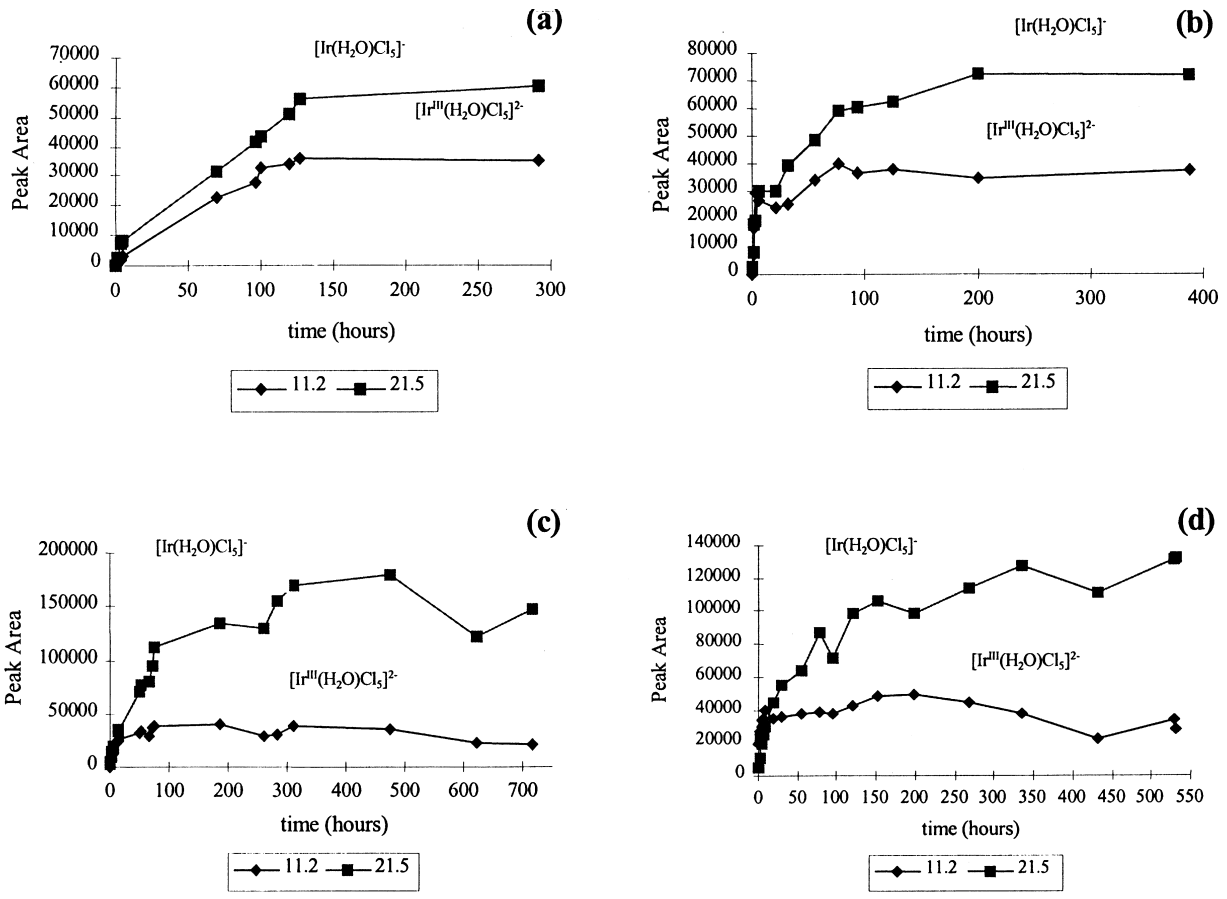

Fig. 3. Evolution of the peak area for species $[Ir(H_2O)Cl_5]^-$ (migration time of 21.5 min) and $[Ir^{III}(H_2O)Cl_5]^{2-}$ (11.2 min) in 1 *M* acid (a), pH = 0.91 (b), 1.95 (c) and 2.68 (d).

presence at pH 3. All the other peaks are attributed to the formation of dimers of the aquated molecules by hydroxo bridges.

Spectra of the different species separated by CZE were obtained and they are given in Fig. 4. No individual spectra of Ir(IV) or Ir(III) species were reported before.

3.3. Spectrophotometric study

In order to support the results obtained by capillary electrophoresis, and to obtain more information about this system, spectrophotometry was also applied. Spectra measured for different time values can be used to estimate the number of species present in solution, e.g., applying the SIBYLA program [18].

Fresh solutions of Ir(IV) at the same proton concentrations as in the CZE studies were prepared and measured with the diode-array spectrophotometer measuring the spectra at fixed time intervals during 24 h.

From Fig. 5 it is possible to see how the spectra changes with time. It indicates also the change of the speciation in solution with time.

3.3.1. Determination of the number of species

SIBYLA is a personal computer program [18], which allows performance of principal component analysis of spectrophotometric data in order to determine the number of species present in solution. Table 3 shows the results of SIBYLA applied to the different solutions studied.

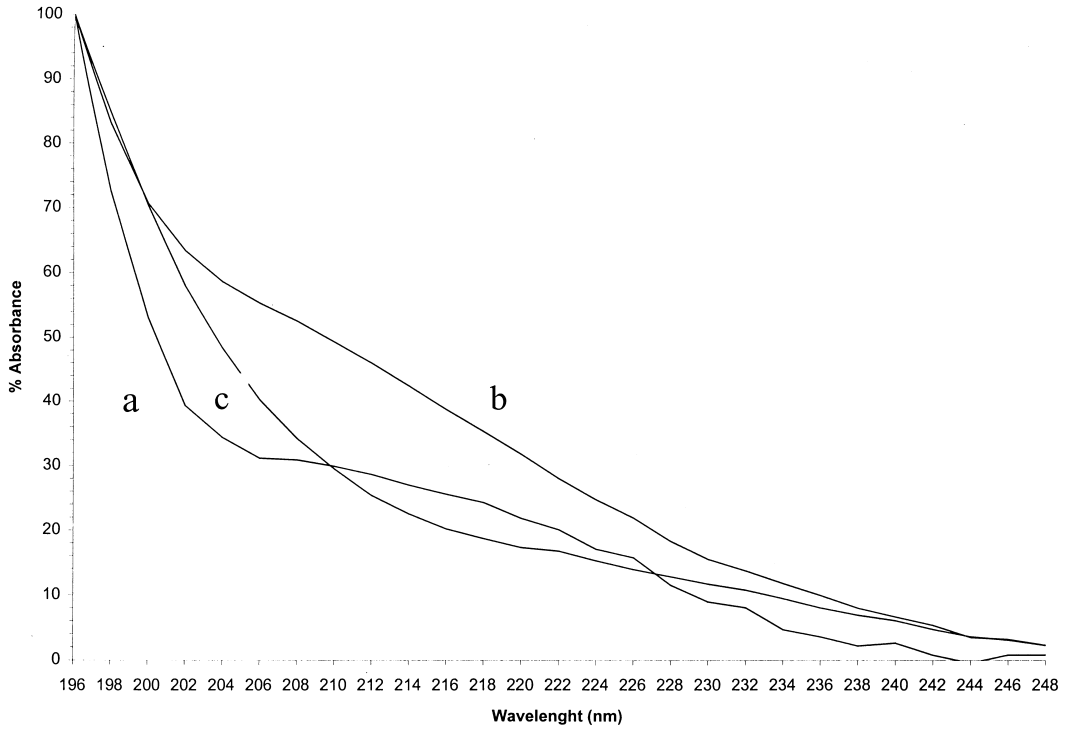

Fig. 4. Absorption spectra of the species with migration time of 8.5 (a), 11.2 (b) and 21.5 min (c), corresponding to $[IrCl_6]^{2-}$, $[Ir(H_2O)Cl_5]^{2-}$ and $[Ir(H_2O)Cl_5]^{-}$ species.

Rank of the matrix was found to be 4 or 5 for most of the criteria. Eigenvalues of the second moment matrix were near to zero for a number of species equal or higher than 5. Values of the trace value minus the sum of the eigenvalues are also near to zero for a number of components equal or greater than 5. Furthermore, almost 100% variability in the data can be explained when the rank of the matrix is equal to 4, how is possible to see from the variance (%) and cumulative per cent variance values. Residual standard deviation also indicates a rank matrix equal to 4, which is possible to see more clearly from Fig. 6. These results are in agreement with the above-discussed results in CZE that indicates more than seven compounds.

During spectrophotometric study a precipitate formation in the solution at pH 3 was observed 5 days after dissolving the substance. It indicates that at a high concentration of Ir, the hydrolysis of the chloro complexes finally goes toward the formation of a nonsoluble compound at pH value equal to or higher than 3.

4. Conclusions

The speciation of Ir(IV) chloro complexes in acidic media is more complicated that was expected. The formation of at least seven to eight species was proved to involve aquo–chloro, hydroxo–chloro complexes and some higher aggregates (probably dimers), accompanied by a partial reduction of Ir(IV) to Ir(III) in the range of proton concentration from 10^{-3} up to 1 *M*, with an additional presence of the reduced species at 1 *M* HCl. The results also indicate that when equilibrium was accomplished the species present in the solution were $[IrCl_6]^{2-}$, $[Ir(H_2O)Cl_5]^{-}$ and $[Ir(H_2O)Cl_5]^{2-}$, only with a high abundance of the last two at pH values equal to or higher than 1.

Spectrophotometry indicates a lower number of

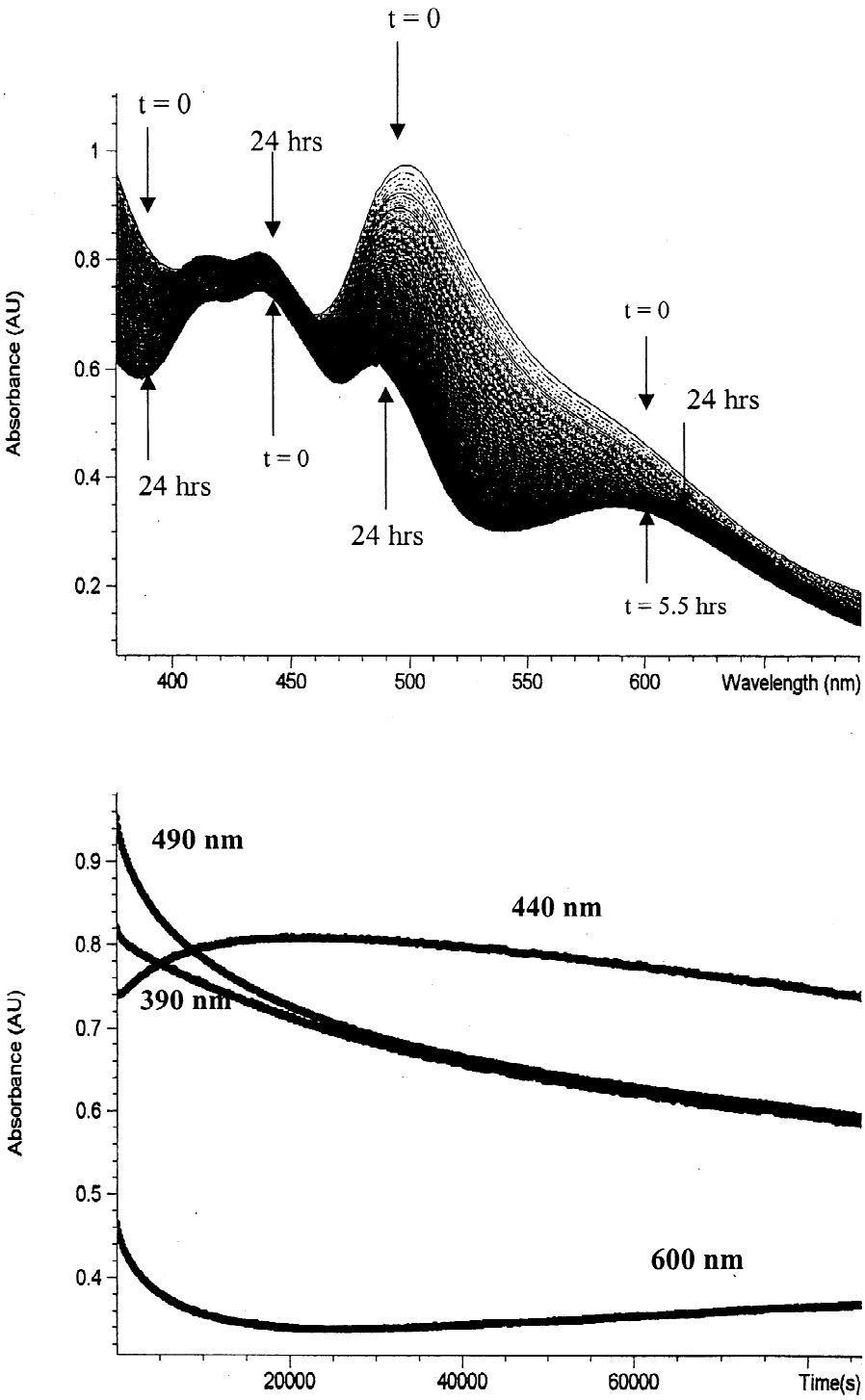

Fig. 5. Evolution of the absorption spectra of an iridium(IV) solution with time. $C_{Ir} = 214$ mg l^{-1}, pH = 2.38, time values: each 5 min during 24 h.

Table 3
Results of factor analysis of spectrophotometric data using the SIBYLA program for the solutions at different acidities

Rank	E.V. ×1000	Sum of E.V. ×1000	Tr−S.E.V. ×1000	Variance (%)	Cum. Var. (%)	D.F.	Resid. S.D. ×1000	IND Malinowski
$[H^+]=1$ *M*								
1	7237.942676	7237.943	31.110688	99.5720	99.5720	49	25.1975	$0.1049\cdot10^{-4}$
2	29.561032	7267.504	1.549656	0.4067	99.9787	48	5.6819	$0.2466\cdot10^{-5}$
3	1.501745	7269.005	0.047911	0.0207	99.9993	47	1.0096	$0.4571\cdot10^{-6}$
4	0.042674	7269.048	0.005237	0.0006	99.9999	46	0.3374	$0.1595\cdot10^{-6}$
5	0.003733	7269.052	0.001504	0.0001	100.0000	45	0.1828	$0.9028\cdot10^{-7}$
6	0.001125	7269.053	0.000379	0.0000	100.0000	44	0.0928	$0.4794\cdot10^{-7}$
7	0.000053	7269.053	0.000326	0.0000	100.0000	43	0.0871	$0.4710\cdot10^{-7}$
8	0.000019	7269.053	0.000307	0.0000	100.0000	42	0.0855	$0.4846\cdot10^{-7}$
9	0.000014	7269.053	0.000293	0.0000	100.0000	41	0.0845	$0.5029\cdot10^{-7}$
10	0.000014	7269.053	0.000279	0.0000	100.0000	40	0.0836	$0.5223\cdot10^{-7}$
pH=1								
1	2829.540646	2829.541	11.976081	99.5785	99.5785	42	16.8862	$0.9573\cdot10^{-5}$
2	11.059639	2840.600	0.916441	0.3892	99.9678	41	4.7278	$0.2813\cdot10^{-5}$
3	0.899470	2841.500	0.016971	0.0317	99.9994	40	0.6514	$0.4071\cdot10^{-6}$
4	0.014463	2841.514	0.002508	0.0005	99.9999	39	0.2536	$0.1667\cdot10^{-6}$
5	0.002366	2841.517	0.000143	0.0001	100.0000	38	0.0613	$0.4242\cdot10^{-7}$
6	0.000009	2841.517	0.000133	0.0000	100.0000	37	0.0600	$0.4386\cdot10^{-7}$
7	0.000009	2841.517	0.000124	0.0000	100.0000	36	0.0588	$0.4535\cdot10^{-7}$
8	0.000006	2841.517	0.000118	0.0000	100.0000	35	0.0581	$0.4740\cdot10^{-7}$
9	0.000006	2841.517	0.000112	0.0000	100.0000	34	0.0573	$0.4957\cdot10^{-7}$
10	0.000006	2841.517	0.000106	0.0000	100.0000	33	0.0566	$0.5196\cdot10^{-7}$
pH=2								
1	*	*	47.638737	99.6239	99.6239	49	31.1804	$0.1299\cdot10^{-4}$
2	45.765076	*	1.873660	0.3613	99.9852	48	6.2478	$0.2712\cdot10^{-5}$
3	1.824364	*	0.049297	0.0144	99.9996	47	1.0241	$0.4636\cdot10^{-6}$
4	0.033496	*	0.015801	0.0003	99.9999	46	0.5861	$0.2770\cdot10^{-6}$
5	0.014954	*	0.000847	0.0001	100.0000	45	0.1372	$0.6776\cdot10^{-7}$
6	0.000035	*	0.000812	0.0000	100.0000	44	0.1358	$0.7017\cdot10^{-7}$
7	0.000033	*	0.000779	0.0000	100.0000	43	0.1346	$0.7281\cdot10^{-7}$
8	0.000031	*	0.000748	0.0000	100.0000	42	0.1335	$0.7566\cdot10^{-7}$
9	0.000030	*	0.000718	0.0000	100.0000	41	0.1323	$0.7872\cdot10^{-7}$
10	0.000029	*	0.000689	0.0000	100.0000	40	0.1313	$0.8203\cdot10^{-7}$
pH=3								
1	***	***	63.108028	99.5877	99.5877	42	38.7630	$0.2197\cdot10^{-4}$
2	60.434786	***	2.673242	0.3948	99.9825	41	8.0747	$0.4804\cdot10^{-5}$
3	2.644136	***	0.029105	0.0173	99.9998	40	0.8530	$0.5331\cdot10^{-6}$
4	0.026640	***	0.002465	0.0002	100.0000	39	0.2514	$0.1653\cdot10^{-6}$
5	0.001617	***	0.000848	0.0000	100.0000	38	0.1494	$0.1035\cdot10^{-6}$
6	0.000051	***	0.000797	0.0000	100.0000	37	0.1468	$0.1072\cdot10^{-6}$
7	0.000051	***	0.000746	0.0000	100.0000	36	0.1439	$0.1111\cdot10^{-6}$
8	0.000041	***	0.000704	0.0000	100.0000	35	0.1419	$0.1158\cdot10^{-6}$
9	0.000041	***	0.000664	0.0000	100.0000	34	0.1397	$0.1209\cdot10^{-6}$
10	0.000041	***	0.000623	0.0000	100.0000	33	0.1374	$0.1262\cdot10^{-6}$

Data: spectra taken in the range 350–680 nm (step 2 nm), with the time interval of 5 min during 24 h.
E.V., eigenvalue; Tr−S.E.V, trace value minus the sum of the eigenvalues; Cum. Var., cumulative percent variance; D.F., degrees of freedom; Resid. S.D., residual standard deviation; IND, Malinowski's empirical indicator function (defined in e.g. Ref. [18]).

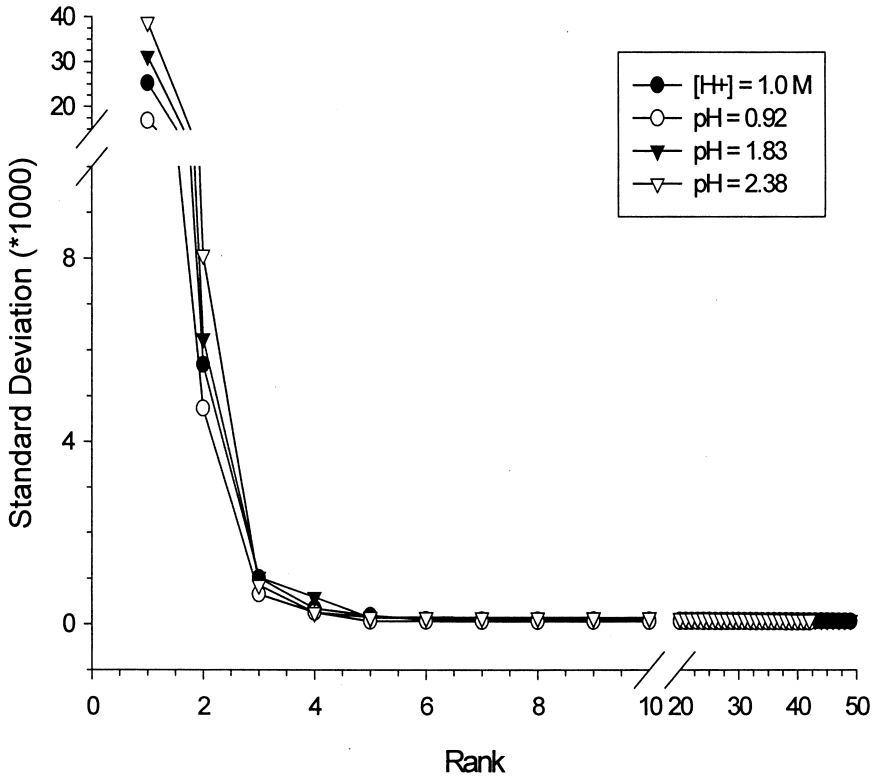

Fig. 6. Results of the principal component analysis. Residual standard deviation (×1000) in front of the freedom degree of the matrix corresponding to the different spectra studied. The junction between the two theoretical straight lines corresponding to each experiment indicates the value of the rank of the absorbance matrix.

species than are really present in the solution, because spectra of the species are similar to each other.

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