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Characterization of chromium (III)-glycine complexes in an acidic medium by UV-visible spectrophotometry and capillary electrophoresis

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ABSTRACT

Since the 2017 REACH restrictions on hexavalent chromium, the aeronautics industries have been seeking substitute processes for chromium plating. So far, use of trivalent chromium-based precursors seems to be the best solution in terms of process adaptation. The development of such processes requires a better understanding of plating bath solution chemistry. More specifically, there is a need to characterize the complexation mechanisms occurring with the chromium (III), since they are responsible for higher electrodeposition efficiency. Chromium (III) complexation occurs under specific conditions, such as in an acidic solution, where chromium hydrolysis takes place, leading to a stable aqua chromium complex, which is suspected to be detrimental to an even deposit. To tackle this issue, a complexing agent is added to destabilize hexaaquachromium complex. It is reported that ligands such as glycine allow the formation of chromium-ligand complexes under specific pH and chromium-ligand ratios. In order to identify and understand the formation of the various complexes, two characterization methods have been tested: UV-visible spectrophotometry, which allows identification of chromium complexes through d-d electronic transition in the UV-Visible range, and capillary electrophoresis as a separation method, coupled with UV-visible detection in order to identify and quantify each species. UV-visible spectrophotometry and capillary electrophoresis analyses revealed that no chromium-glycine complex was observed for pH lower than 2, which is the regular condition for electrodeposition. Only a higher Gly:Cr ratio and/or pH > 2.4 (i.e. pK_{a1} of glycine) made it possible to observe glycine complexes in solution. As these conditions could be met during electrodeposition near the substrate/electrolyte interface, it is highly likely that chromium depletion, together with the pH increase that occurs, could favor the formation of glycine complexes at the interface, which have been reported as being required to achieve homogeneous chromium deposits.

1. Introduction

Hard chromium plated surfaces are versatile, achievable on a broad range of substrates, and widely used to confer specific properties such as antiwear, anticorrosion and hardness on pieces [1–3]. In conventional chromium coating, hexavalent chromium-based electrolytes are used in an electrochemical bath. Since 2017, the European REACH Regulation has regulated hexavalent chromium use because of its carcinogenic, mutagenic and reprotoxic hazards [4], as such surface treatments in the automotive, aeronautic and spatial fields expose users to Cr(VI) toxicity, as well contaminating the environment during the plating process.

To address this issue, multiple substitution processes have been studied: changing the deposition method to thermal spraying, vapor deposition or electrodeposition with trivalent chromium plating baths [1–3,5–7].

Trivalent chromium can easily replace hexavalent chromium plating with less process modification. The most usual chromium (III) precursor is chromium (III) chloride, leading to more homogeneous deposits, as it is more prone to form complexes [8] than other chromium precursors, such as sulfate or perchlorate chromium salts. Chromium chloride dissolves in an acidic aqueous solution to form $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$, $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ [9–15]. Gaspar [10] & Glod [11] reported that first $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ hydrolyzes quickly to $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ which stabilizes to $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, the thermodynamically more stable complex in acidified water. For this reason, electrochemical deposition is usually performed with the addition of a complexing agent, which is assumed to destabilize the chromium aqua-complex [9,16–18] and hence achieve an even chromium deposit. The role of such complexing additives has still not been fully unraveled. It is thought that the complexing agent plays subtle roles, such as improving the charge transfer efficiency of the

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electrodeposition of Cr [19], or acting as a buffering agent, stabilizing the pH at the electrode/electrolyte interface and lowering the surface energy of the electrode [20–22]. Multiple complexing agents have been investigated. Oxalic acid [9,23,24] and urea [24–26] have been studied, but two of the most widely used have been glycine [9,18,22–24,27–37] and formic acid [9,23–26]. Glycine has turned out to be the best candidate to achieve a good quality deposit. It complexes chromium easily. Inorganic salts are also added to improve the metal deposit. Sodium chloride is used to increase electrolyte conductivity [18,23,27–33,35,38], aluminum chloride to improve the shine and lifespan of the electrolyte [18,23,27,29,30,37] and boric acid [18,25–30,32–39], or ammonium chloride [18,27–34,36–38] are added as a pH buffer to enhance the quality of the metal film deposit. It is worth noting, in the case of glycine, that a pH range lower than 2 is required to achieve homogeneous chromium coating [9,18,22,23,27–37,40]. Overall, the role of glycine is not clearly evidenced and the complex species are not clearly defined at the pH of chromium electrodeposition.

In order to get a better insight into the role of glycine, this work is meant to point out the different chromium complexes present under acidic conditions. Although more even deposits are obtained in low pH media, it has been reported in the literature that chromium-glycine complexes are generally obtained at a pH higher than 3 [37,41–46]. In this work, electrolyte formulation was selected according to the literature [18,23,28,29,33,34], with CrCl₃ as chromium precursor and glycine as the complexing agent.

To shed light on the role of glycine, different analyses were combined involving UV–Visible spectrophotometry to identify and quantify chromium species, and capillary electrophoresis to separate and go further in the identification of all the species present.

2. Materials and methods

2.1. Electrolyte formulations

Table 1 displays the three formulations studied according to their glycine:chromium (III) molar ratio, 0:1 (without); 1:1 and 1:0.25 together with the concentration of other additives. All reagents were of analytical grade purity: chromium (III) chloride (CrCl₃·6H₂O purum p. a., ≥ 98.1%) from Sigma Aldrich CAS 10060–12-5), glycine (NH₂CH₂COOH ReagentPlus, ≥ 99% (HPLC) from Sigma Aldrich CAS 56–40-6), sodium chloride (NaCl BioXtra, ≥ 99.5% from Sigma Aldrich CAS 7647–14-5), ammonium chloride (NH₄Cl Puratronic, 99.999% from Alfa Aesar CAS 12125–02-9) and aluminum chloride (AlCl₃·6H₂O ReagentPlus, 99% from Sigma Aldrich CAS 7784–13-6). Components were dissolved into ultrapure water (12 MΩ·cm) at ambient temperature and acidified with HCl (37%) down to pH < 2. Then the electrolyte was heated for 1 h at 80 °C.

2.2. Characterization measurements

The UV–visible absorption spectra were recorded between 200 nm and 900 nm, using the 1 mm quartz cells on a Perkin Elmer lambda 365 nm spectrometer. Results were then analyzed using Peakfit v4.12 (Sigmplot [Systat Software Inc] n°:4500429198), a spectral deconvolution software. A Gaussian Area fit was selected for deconvolution. The deconvolution results and species proportions were calculated with an uncertainty of 10%.

Table 1
Electrolyte Bath compositions.

	CrCl ₃ ·6H ₂ O	Glycine	NaCl	NH ₄ Cl	AlCl ₃ ·6H ₂ O
Gly:Cr molar ratio	Concentration in mol L ⁻¹				
0:1	0.5–1	–	0.5–1	0.5–1	0.1 – 0.5
1:1	0.5–1	0.5–1	0.5–1	0.5–1	0.1 – 0.5
1:0.25	0.1 – 0.2	0.5–1	0.5–1	0.5–1	0.1 – 0.5

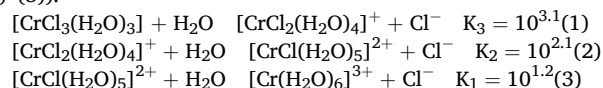
Capillary electrophoresis of the solution was undertaken using a Beckman P/ACE System MDQ instrument. Beckman Coulter eCap capillaries were used, with a total length of 70 cm, effective length of 50 cm, 75 μm I.D. and 375 μm O.D. (338454). The buffering agent was a mixture of 20 mmol.L⁻¹ *ortho*-phosphoric acid (LiChropur for HPLC) and 7 mmol.L⁻¹ of imidazole resulting in pH = 2.4. Sample injection was performed in 5 s at a voltage of 1 kV, while the electrophoretic voltage was set at 25 kV. The solutions were diluted 20 times with buffer before being analyzed. The separated electrolytes were detected indirectly by a UV–Visible absorption detector.

3. Results and discussion

In order to characterize the complexes in solution, UV–visible absorption spectra of electrolytes at pH < 2 were recorded, without (Gly:Cr 0:1) and with glycine (Gly:Cr 1:1).

Both electrolytes were measured freshly prepared at room temperature and after 1 h heating at 80 °C (Fig. 1. Vertical lines noted A, B and C represent λ_{max} reference data. In the case of the freshly prepared electrolyte 0:1 (Fig. 1 a - blue dotted line), absorption bands are observed at λ₁ = 446 and λ₂ = 634 nm, corresponding to [CrCl₂(H₂O)₄]⁺ based on literature data (λ₁ = 450 nm, λ₂ = 635 nm [13] spotted by vertical lines C). However, the 1:1 electrolyte (Fig. 1 a - black line) has the analogous absorption bands at λ₁ = 438 and λ₂ = 628 nm, corresponding to a mixture of [CrCl(H₂O)₅]²⁺ (λ₁ = 430 nm, λ₂ = 605 nm [13] comparatively depicted as vertical lines B and C, respectively) and [CrCl₂(H₂O)₄]⁺ complexes. On the other hand, in the case of heated electrolytes (Fig. 1b, absorption bands are located at λ₁ = 422 nm and λ₂ = 594 nm, for the 0:1 electrolyte and at λ₁ = 420 nm and λ₂ = 588 nm, for the 1:1 electrolyte, respectively. These values indicate that both electrolytes contain a mixture of [CrCl(H₂O)₅]²⁺ and [Cr(H₂O)₆]³⁺ (λ₁ = 407 and λ₂ = 575 nm). The heating of the solution at pH < 2 sets off the formation of the hexaaquachromium (III) complex formation, rather than the formation of the chromium-glycine complexes, as previously reported [18,25,29,44].

These shifts in λ_{max} can be ascribed to the typical hydrolytic ligand exchange on the Cr(III)Cl₃ complex when it is dissolved in an acidic aqueous medium and is in accordance with the literature [25–29]. Chromium chloride dissolution involves thermodynamic equilibria (Eqs. (1)–(3)):



Because the K₁, K₂ and K₃ values are between 10 and 10⁴, equilibrium is expected to evolve towards [Cr(H₂O)₆]³⁺ formation.

Zeng [12] got similar results at pH 2.5 when formic acid was used for electrodeposition. They reported two absorption bands at λ₁ = 441 and λ₂ = 640 nm, corresponding to the [CrCl₂(H₂O)₄]⁺ complex, for freshly prepared Cr(III)Cl₃ solution. Upon heating the same solution for 1 h, they observed the corresponding two absorptions at λ₁ = 412 and λ₂ = 578 nm, corresponding to [Cr(H₂O)₆]³⁺. When glycine was used in place of formic acid under similar conditions, some researchers have reported the formation of glycine Cr(III) complexes [18,27–29,33,36], but none have presented proof of the existence of the complexes. This prompted us to carry out a more in-depth analysis of the identity of the species in acidic aqueous Cr(III)Cl₃ solutions (as prepared or after heating) with and without glycine.

The pH value of the electrodeposition bath is a key point for the formation of metal-glycine complexes [41–43,46–48]. Shuttleworth and Sykes [48] reported that coordination of the carboxylate group occurs at pH values lower than 4; whereas coordination of the amino groups of glycine is only favored at pH values higher than 7. In aqueous solution, glycine can exist as glycinium (indicated GlyH₂⁺) under pH 2.4, zwitterion (indicated Gly⁻H⁺) at pH of between 2.4 and 9.8, and glycinato (indicated Gly⁻) beyond 9.8 [47], as summed up in Fig. 2. Complexation of Gly⁻ as a bidentate ligand is the most usual mode of coordination in a

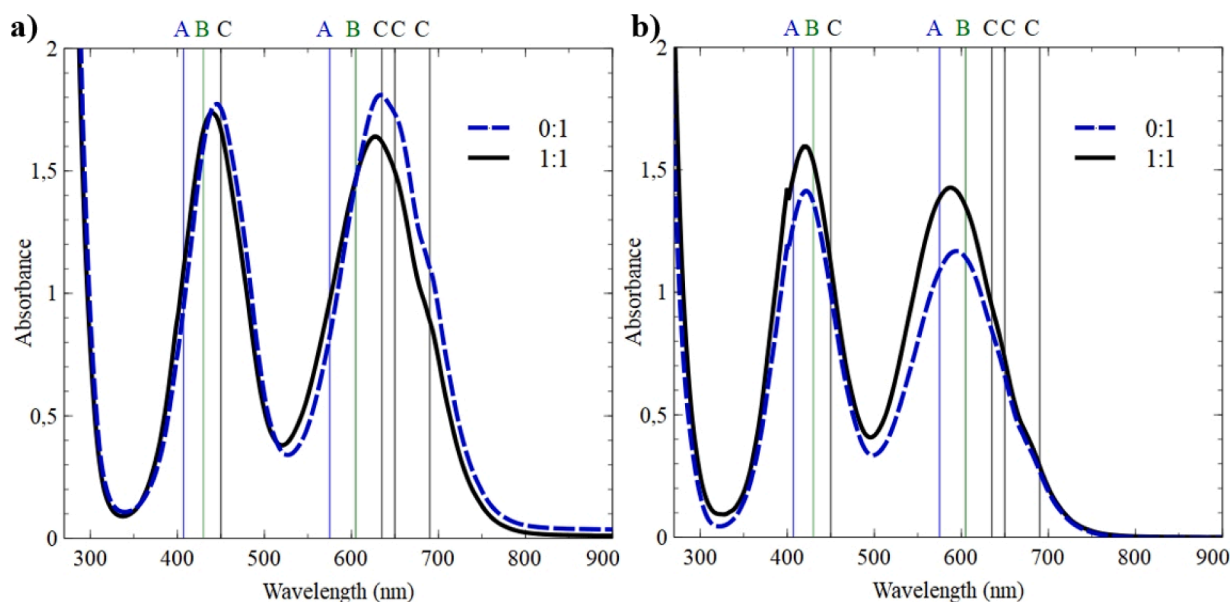


Fig 1. UV-visible absorbance spectra of 0:1 (blue dotted line) and 1:1 (black line) electrolytes freshly prepared at room temperature (a) and heated for 1 h at 80 °C (b). Vertical lines A, B and C represent λ_{\max} reference data of: $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (blue line), $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ (green line) and $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ (black line), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

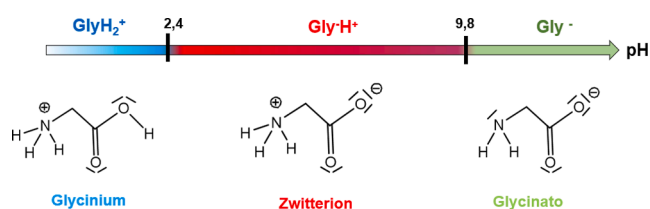


Fig. 2. Glycine forms in different pH ranges.

basic medium, whereas the $\text{Gly}^- \text{H}^+$ zwitterionic form can coordinate to the metal via one bond (monodentate) or two bonds (bidentate). The glycinium species (GlyH_2^+) is the form least likely to coordinate, since neither the carboxylic acid nor ammonium functional groups can coordinate easily to the metal ions.

When glycine and $\text{Cr}(\text{III})\text{Cl}_3$ aqueous complexes are mixed under acidic conditions, ligand exchanges may occur leading to different glycine-(aqua/Cl)Cr(III) complexes. Such complexes have been reported in the literature, [12,13,15,41–44,46,49] via UV-visible spectrophotometry analysis.

Fig. 3 presents the absorbance wavelength maxima of chromium complexes collected in the literature. There is a general agreement that $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ and $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ are species associated with the second (longer wavelength) absorption band at $\lambda_2 \geq 570$ nm. In the case of chromium-glycine complexes ($[\text{Cr}(\text{gly})_3]$, $[\text{Cr}(\text{gly})_2\text{OH}]_2$, $[\text{Cr}(\text{gly})_2(\text{H}_2\text{O})_2]^+$ and $[\text{Cr}(\text{gly})(\text{H}_2\text{O})_4]^{2+}$), the maxima of their second absorption band λ_2 values are lower than 570 nm. The higher the number of glycine ligands coordinated to the Cr(III) ion, the shorter the absorption wavelength maximum of the second band. Moreover, in the case of chromium-glycine complexes, the first absorbance band is always less intense than the second, as $A_{\lambda_1}/A_{\lambda_2} < 1$. In the case of chromium aqua or chloro complexes, the first absorbance band is always more intense than the second, as $A_{\lambda_1}/A_{\lambda_2} > 1$.

For glycine complexes, some values are very dispersed and close to $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ values, like for the $[\text{Cr}(\text{gly})_2(\text{H}_2\text{O})_2]^+$ complex. Here, we proposed that the complex obtained by Uddin at pH 3.76 [43], characterized by two absorptions at $\lambda_1 = 409$ nm and $\lambda_2 = 553$ nm, should be assigned to $[\text{Cr}(\text{glyH})(\text{H}_2\text{O})_5]^{3+}$ and not to $[\text{Cr}(\text{gly})_2(\text{H}_2\text{O})_2]^+$ [43]. In the same way, the complex noted as $[\text{Cr}(\text{gly})(\text{H}_2\text{O})_4]^{2+}$ [43] and

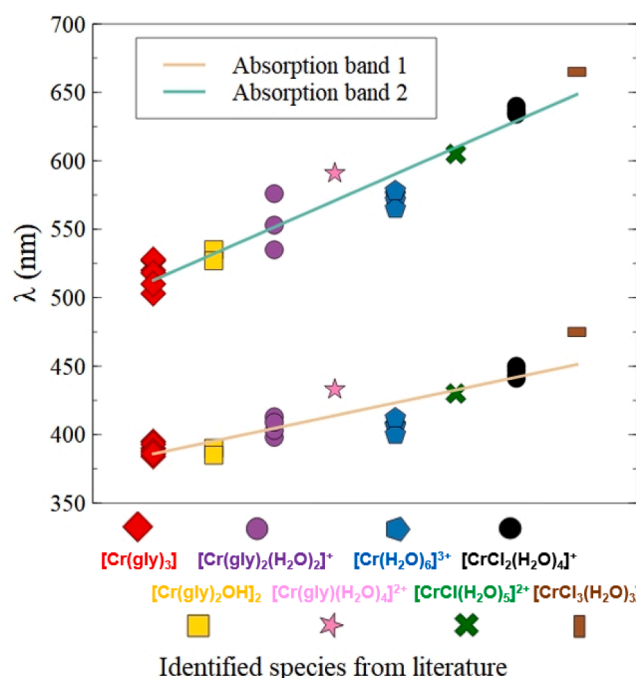


Fig. 3. Absorption data for aqua, chloro and glycinato chromium complexes (obtained at pH > 3) as reported in the literature [12,13,15,41–44,46,49].

obtained at pH 3.07, characterized by two absorptions at $\lambda_1 = 433$ nm and $\lambda_2 = 591$ nm, corresponds to a mixture of $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ ($\lambda_1 = 430$ nm and $\lambda_2 = 605$ nm) and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ($\lambda_1 = 407$ nm, $\lambda_2 = 575$ nm) [13].

Authors have reported the existence of different forms of chromium-glycine complexes at pH higher than 2.4, where the glycinium species becomes negligible [12,13,15,41–44,46,49]. The ligand coordination equilibrium is expected to be different for a pH below 2.4 (i.e. pK_{a1} of glycine), normally used in chromium-glycine electrodeposition baths. Such a pH condition is not in favor of chromium complexation with glycine, with glycinium and zwitterionic forms prevailing. According to

Barneja [44], at pH 3.2–4, glycine complexation to form the $[\text{Cr}(\text{glyH})(\text{H}_2\text{O})_5]^{3+}$ complex is very slow between 35 and 50 °C. On the other hand, at pH 8.5–9.5, they observed very rapid pre-equilibrium forming the ion-pair $\text{Cr}(\text{H}_2\text{O})_6^{3+} \bullet \text{Gly}$. Abdullah also studied Cr(III) coordination of glycine under zwitterionic form (pH 3–3.8), he observed chromium glycine complex under $[\text{Cr}(\text{glyH})(\text{H}_2\text{O})_5]^{3+}$ [50].

However, Baral [18] and McDougall [29] reported that glycine is coordinated to chromium at pH < 2. At pH 0.5, they observed a slight shift to shorter wavelength between chromium chloride solution and chromium-glycine mixture: (λ_1 : 426 to 422 nm and λ_2 : 596 to 589 nm without and with glycine respectively) [18]. They suggested that this slight shift is attributed to chromium-glycine complex, enforced by boiling for 30 min.

According to these different findings — from the literature and from our preliminary results — chromium-glycine complexation at low pH still requires clarification. The effect of Gly:Cr ratios and pH were studied in order to investigate the formation of Cr(III)-glycine complexes as described in some of the literature [41,43]. Ratios Gly:Cr = 0:1, 1:1 and 1:0.25 were prepared at pH < 2 and > 2. The latter pH is expected to favor the zwitterionic or glycinato forms, known to coordinate to chromium (III) [41,48].

To gain more insights, capillary electrophoresis with indirect UV-Visible detection was performed in order to determine the number of species in each electrolyte. Detection was performed in the indirect mode using Phosphoric acid/imidazole buffer, as reported by A. Gaspar [10]. Figs. 4 and 5 show the electrophoregrams of each precursor for migration time identification.

In Fig. 4, all the electrophoregrams have a positive peak at around 2.4 min corresponding to the buffer signal, NH_4Cl solution reveals a negative peak at around 3 min corresponding to the NH_4^+ cation, Na^+ cation appears with the migration time of 3.8 min, whereas in the glycine solution a negative peak around 8.5 min is assigned to the GlyH_2^+ cation. In the case of AlCl_3 solution, no peak was observed. Efforts were intended to identify free Al^{3+} , but in these conditions only a low wave was observed around 6 min. This position is in agreement with the results of Göttelein [51], and was confirmed by analysis of more concentrated solution but resulted in worse separation of other compounds of the electrolyte. To identify the different complexes of chromium(III) in HCl solution, three electrophoregrams were recorded as a function of time, after 30 min, 2 h and 24 h after dissolution in the buffer. These electrophoregrams are presented in Fig. 5. Each electrophoregram revealed a positive peak due to the buffer at 2.4 min. At a

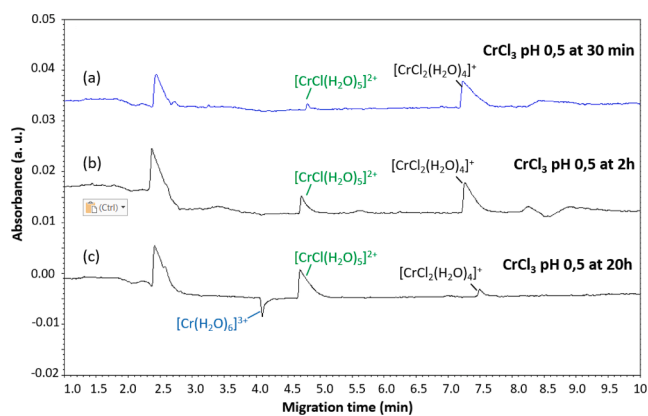


Fig. 5. Electrophoregrams of CrCl_3 pH 0.5 at $t = 30$ min, 2 h and 20 h.

lifetime of 30 min, the solution exhibited a small positive peak at 4.7 min and a large positive peak at 7.2 min, characterized by maximum absorbance at 200 nm and 220 nm respectively. According to A. Gaspar [10], these peaks are assigned to chloroaquachromium(III) complexes, $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ and $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ respectively. The signal attributed to $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ grows from $t = 30$ min to $t = 20$ h to the detriment of the $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ signal. Moreover, at $t = 20$ h a negative peak appeared at 4.2 min assigned to $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, according to A. Gaspar.

Peak positions shift slightly over days, due to electrokinetic injection repeatability. In order to assess our assignment, electrophoregrams were recorded in triplicate. Supplementary material presents the repeatability of the injection over one day in Fig. S1.

Fig. 6 presents electrophoregrams of the 0:1, 1:1 and 1:0.25 electrolytes prepared at pH < 2, with solutions freshly prepared at room temperature in a) and heated for 1 h at 80 °C as prepared in b). All the electrophoregrams exhibit the peaks corresponding to NH_4^+ (superimposed on the buffering agent signal) and Na^+ . For the 1:1 and 1:0.25 electrolytes, the peak of GlyH_2^+ appears between 8 and 9.5 min. The freshly-prepared electrolytes at room temperature (Fig. 4a contain the $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ and $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ complexes (5 and 7.5 min peaks respectively). For electrolytes freshly-prepared at room temperature, except the peak of GlyH_2^+ , the electrophoregrams for the 1:1 and 1:0.25 electrolytes are the same as for the 0:1 electrolyte, with no peaks observed corresponding to the glycine complexes. This means that in the freshly prepared electrolyte, no chromium-glycine complexes were

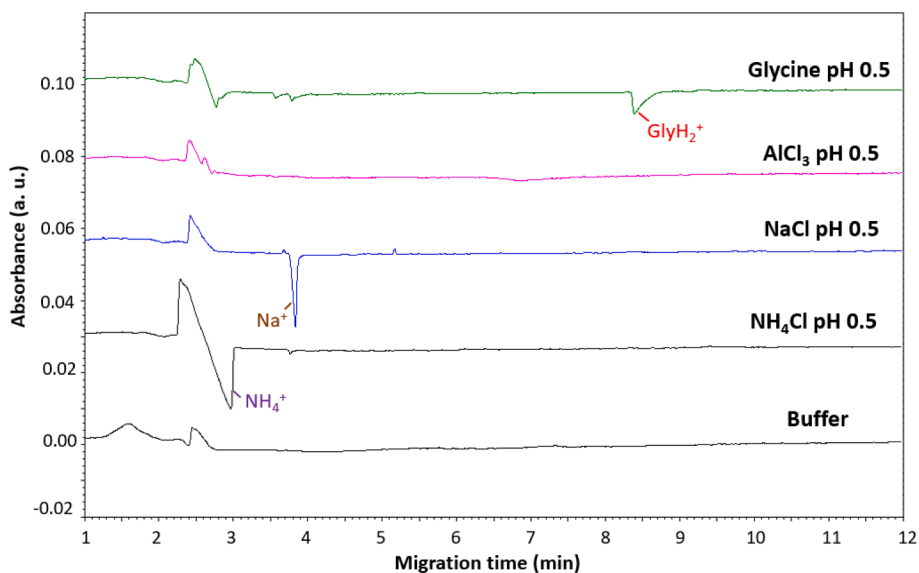


Fig. 4. Electrophoregrams of Glycine, AlCl_3 , NaCl , NH_4Cl pH 0.5 and buffer.

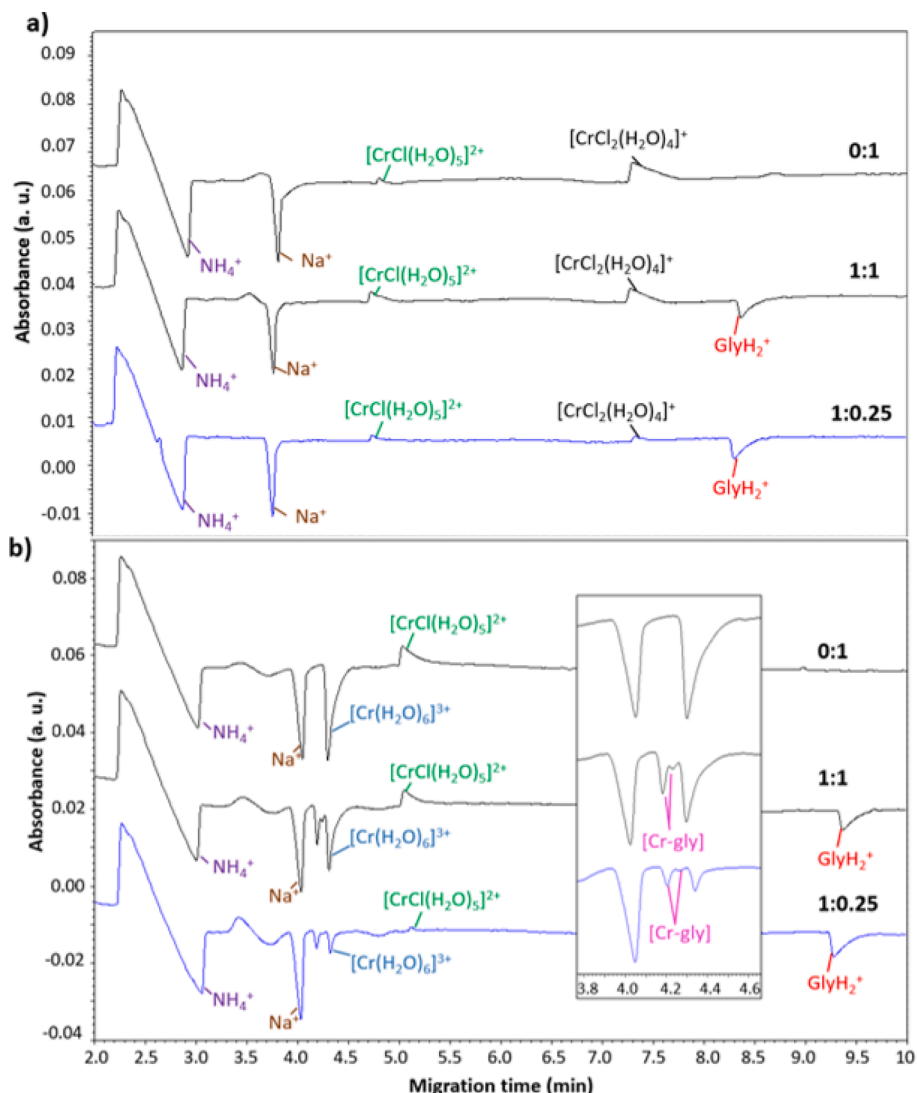


Fig. 6. Electrophoregrams of electrolytes 0:1, 1:1 and 1:0.25 prepared at pH < 2, freshly prepared at room temperature (a) and heated 1 h at 80 °C (b).

formed, even for the 1:0.25 Gly:Cr molar ratio.

After heating the 0:1 electrolyte for 1 hour at 80°C, the electrophoregram (Fig. 4b) clearly reveals the presence of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ at 4.4 min, to the detriment of $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$, which has vanished. This observation is in line with the chloro-aqua ligands exchange at elevated temperatures [10,11]. As proven by Buglyo and Glod [10,11] using capillary electrophoresis and H_3PO_4 buffer at pH 2.4, at $t = 2\text{h}$, $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ and $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ complexes are predominant over $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. They also noticed that after 60h, $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ disappeared due to the formation of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. When the 1:1 and 1:0.25 electrolytes were heated, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ formed as $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ was depleted, but in these cases, compared to the 0:1 electrolyte, two small signals appeared at 4-5 min, between the Na^+ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ peaks. These peaks are likely correlated with the presence of glycine. As a result, Cr-gly complexes were observed. It is possible that these two peaks were due to the presence of chromium (III)-glycine complexes, as $[\text{Cr}(\text{glyH})(\text{H}_2\text{O})_5]^{3+}$ and $[\text{Cr}(\text{GlyH})_2(\text{H}_2\text{O})_4]^{3+}$. With separation being performed at pH 2.4, the formation of such complexes cannot be ruled out.

This hypothesis is confirmed by the increase in the signal when the glycine proportion increases. In the 1:1 electrolyte, the peak assigned to the Cr-Glycine complex is very small compared to those of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. On the other hand, in the 1:0.25 electrolyte, the peak assigned to a Cr-Glycine complex is almost as high as the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ one. This result

suggests a correlation between the concentrations of glycine and its chromium complex.

The possible complexation observed between chromium and glycine is a consequence of the slight increase in the pH (2.4) at which the experiments were conducted.

Absorbance ratios ($A_{\lambda_1}/A_{\lambda_2}$) were calculated to assign and identify the predominant complexes in each electrolyte. The absorbance ratios are usually < 1 for the chromium-glycine complexes and $A_{\lambda_1}/A_{\lambda_2} > 1$ for chromium aqua or for chloro complexes. For the heated electrolytes, the chromium chloride and hexaqua complexes predominated at pH < 2, for all the Gly:Cr molar ratios (0:1 ; 1:1 or 1:0.25) and at pH > 2 for the 1:1 Gly:Cr electrolyte. The chromium-glycine complex species seemed predominant only for the 1:0.25 Gly:Cr electrolyte when pH was higher than 2.

UV-Visible spectra of 1:1 and 1:0.25 electrolytes heated for 1 hour at 80°C at pH < 2 and at pH > 2 are compared in Fig. 7a and 7b. As observed in Fig. 7a, for pH < 2, absorbance peaks are located at 422 and 594 nm for the 0:1 electrolyte; at 420 and 588 nm for the 1:1 electrolyte, and at 414 and 580 nm for 1:0.25 electrolyte. These values are consistent with the presence of $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, which are expected to be predominant for the 0:1 and 1:1 ratios.

On the other hand, for pH > 2, the absorbance peaks (Fig. 7b) have shifted to 420 and 576 nm for the 1:1 electrolyte and to 416 and 568 nm for the 1:0.25 electrolyte. This shift is assumed to be related to the

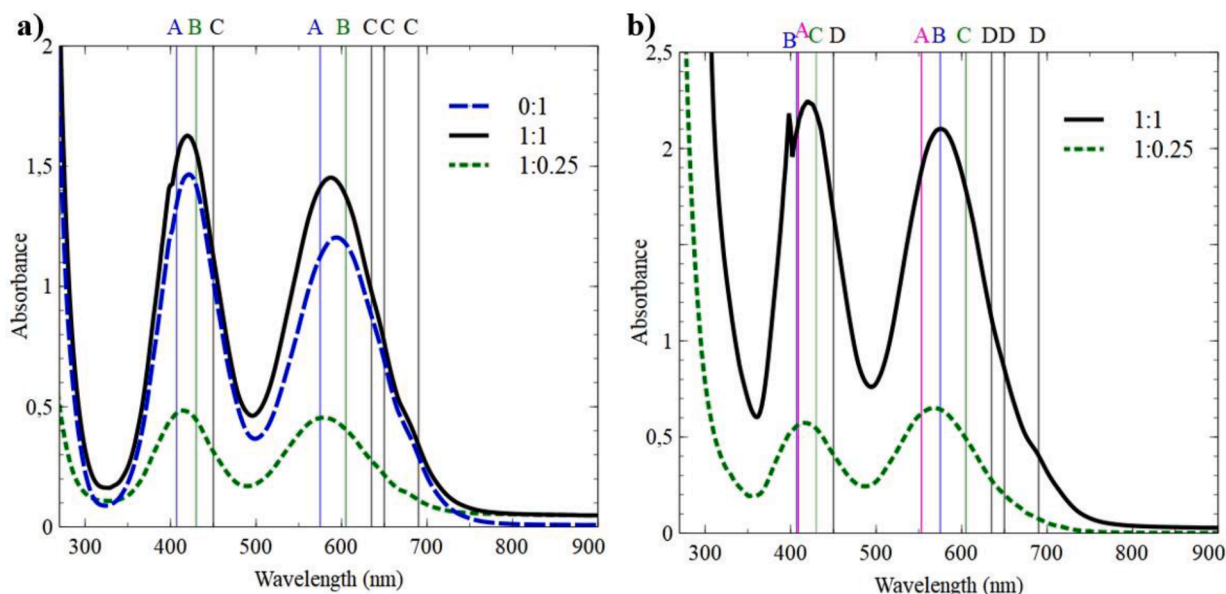


Fig. 7. UV-visible absorbance spectra of 0:1 (blue dotted line), 1:1 (black line) and 1:0.25 (green dotted line) at pH < 2 (a) and pH > 2 (b) after heating electrolytes for 1 h at 80 °C. Vertical lines noted A, B, C and D represent reference data of respectively: $[\text{Cr}(\text{glyH})(\text{H}_2\text{O})_5]^{3+}$ (pink line), $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (blue line), $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ (green line) and $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ (black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

presence of other complexes, likely involving glycine, since at pH > 2, it is expected to be present in its zwitterionic form, as depicted in Fig. 2. According to the literature [41–43,46] and present results, the 1:0.25 electrolyte spectrum is supposedly a mixture of $[\text{Cr}(\text{glyH})(\text{H}_2\text{O})_5]^{3+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, whereas the 1:1 electrolyte spectrum is assumed to be a mixture of the chloro and aqua complexes $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$.

Li et al. [52] studied [L]:[Cr] ratio and pH variations, with $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ as chromium salt and glycine as the ligand. For the Gly:Cr ratio = 2:1, they reported that pH was raised from pH 2.05 to 5, and that λ_2 decreased from 576 to 567 nm. They attributed this variation to $[\text{Cr}(\text{gly})(\text{H}_2\text{O})_4]^{2+}$ or $[\text{Cr}(\text{gly})(\text{H}_2\text{O})_3(\text{OH})]^+$ formation. Moreover, they observed at pH 2.65 that absorption peaks (λ_1 and λ_2) shifted toward lower wavelengths, as glycine concentration increased from the Gly:Cr ratio > 1:1. They concluded that $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ turns to $[\text{Cr}(\text{gly})(\text{H}_2\text{O})_4]^{2+}$. In addition, at pH = 2.65 when the Gly:Cr is 2.5:1, the absorption intensity fell off, indicating that $[\text{Cr}(\text{gly})(\text{H}_2\text{O})_4]^{2+}$ species were being transformed into other species, such as $[\text{Cr}(\text{gly})_2(\text{H}_2\text{O})_2]^+$, leading to a decrease in the concentration of the electroactive chromium complexes.

The same observation was obtained here, which is in line with the fact that both a specific pH and L:Cr ratio are needed to obtain Cr-glycine complexes. Nevertheless, between pH 2 and 5, according to Fig. 2, monodentately-coordinated $[\text{Cr}(\text{glyH})(\text{H}_2\text{O})_5]^{3+}$ is supposed to be present, not $[\text{Cr}(\text{gly})(\text{H}_2\text{O})_4]^{2+}$.

To untangle this, the spectra of the 0:1 and 1:1 electrolytes at pH < 2 were deconvoluted (Fig. 8 — and deconvoluted spectra of 1:0.25 electrolyte pH < 2 and 1:1; 1:0.25 electrolytes pH > 2 are given in S2-S3. $A_{\lambda_1}/A_{\lambda_2}$ ratios were conserved according to values references [13,41]. From these deconvolutions, proportions of each complex were calculated and reported in Fig. 9.

In the case of the 0:1 electrolyte, heated for 1 h at 80 °C and at pH < 2, the deconvolution (Fig. 8a) reveals the coexistence of $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$, $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. This result is in accordance with the literature [10,11]. In the case of the 1:1 electrolyte heated for 1 h at 80 °C and at pH < 2, the deconvolution (Fig. 8b) still reveals the coexistence of the same three complexes, Although $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ still predominates, a larger proportion of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ has formed compared to the 0:1 electrolyte.

Fig. 9 presents the proportions of complexes over time from spectra deconvolution results. As observed, with and without heating, $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ are predominant over the other complexes in each electrolyte. Without heating, only the chloro and hexaqua chromium complexes are present in the 1:1 and 1:0.25 electrolytes, revealing the chloro-aqua ligand exchange. With heating, a non-significant quantity (10%) of $[\text{Cr}(\text{glyH})(\text{H}_2\text{O})_5]^{3+}$ shows up in the 1:1 electrolyte after 7 days. In the case of the 1:0.25 electrolyte, a larger quantity of $[\text{Cr}(\text{glyH})(\text{H}_2\text{O})_5]^{3+}$ can be found (25%±10%) after 7 days.

Heating of the Cr(III)/glycine electrolytes at pH < 2 for one hour at 80 °C favors formation of chromium-glycine complexation, preferentially for the ligand:metal 1:0.25 ratio. However, the concentration of glycine complex remains low, compared to the other complexes — only 15–35% at pH < 2 and with a Gly:Cr ratio ≥ 1:1.

To sum up, heating Cr(III)-glycine electrolyte for one hour at 80 °C favors the formation of chromium-glycine complexes. But at pH < 2, the concentration of these complexes is quite low compared to chromium chloro and aqua complexes (15–35% vs 40–50%). The absorption band studies revealed that the higher the Gly:Cr ratio, the higher the content of chromium-glycine complexes. It is worth noting that electrodeposition of Cr from this solution mixture is highly likely to have similar Cr complex composition at the interfacial regions to that deduced from the results of this study. A lower chromium content, as compared to glycine, and higher pH value, favors the formation of chromium-glycine complexes. The addition of glycine is required to achieve homogeneous chromium deposits [18,27–29,31–33,36].

4. Conclusion

UV-visible absorption spectrophotometry and capillary electrophoresis analyses, were used to identify the chromium glycine complexes associated with an aqueous solution of Cr(III) at pH lower than 2.

UV-visible absorption spectra of a chromium-glycine electrolyte at pH < 2 revealed that, at room temperature and for both the 1:1 and 1:0.25 ratios, only the chromium chloride and hexaqua chromium complexes were found. It was found that chromium glycine complexes showed up only after heating for 1 h at 80 °C. For the 1:1 ratio, glycine coordinated species are negligible — 10% of $[\text{Cr}(\text{glyH})(\text{H}_2\text{O})_5]^{3+}$; in the case of the 1:0.25 ratio, 25% of $[\text{Cr}(\text{glyH})(\text{H}_2\text{O})_5]^{3+}$ was observed.

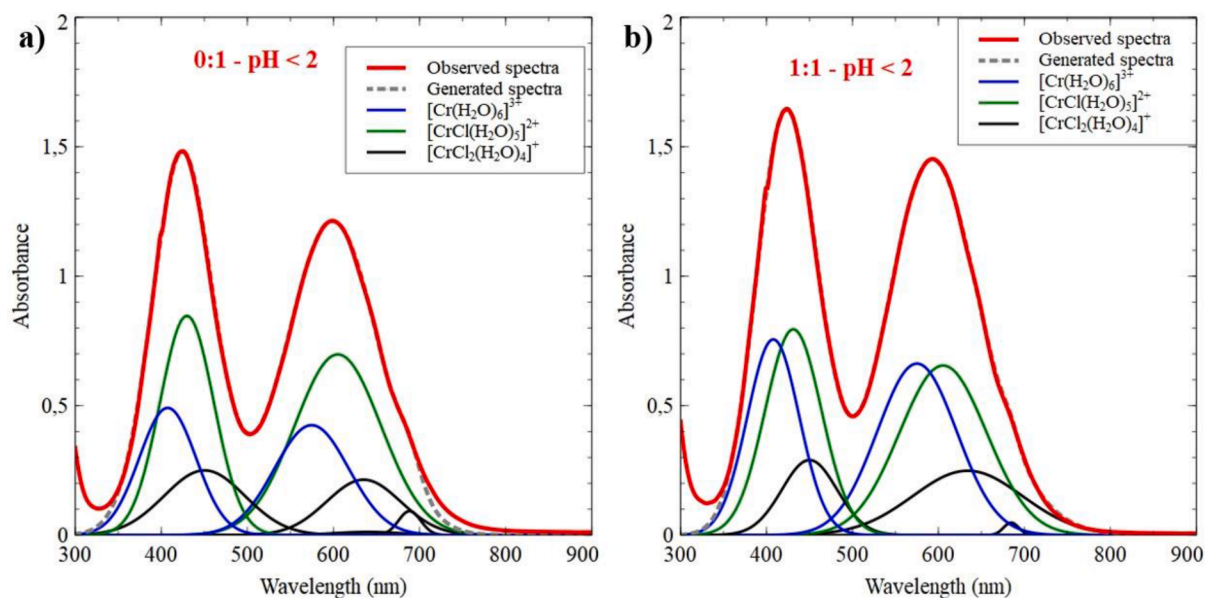


Fig. 8. UV-Visible deconvoluted spectrum of 0:1 electrolyte (a), 1:1 electrolyte (b), at pH < 2 each heated for 1 h at 80 °C and aged 2 h.

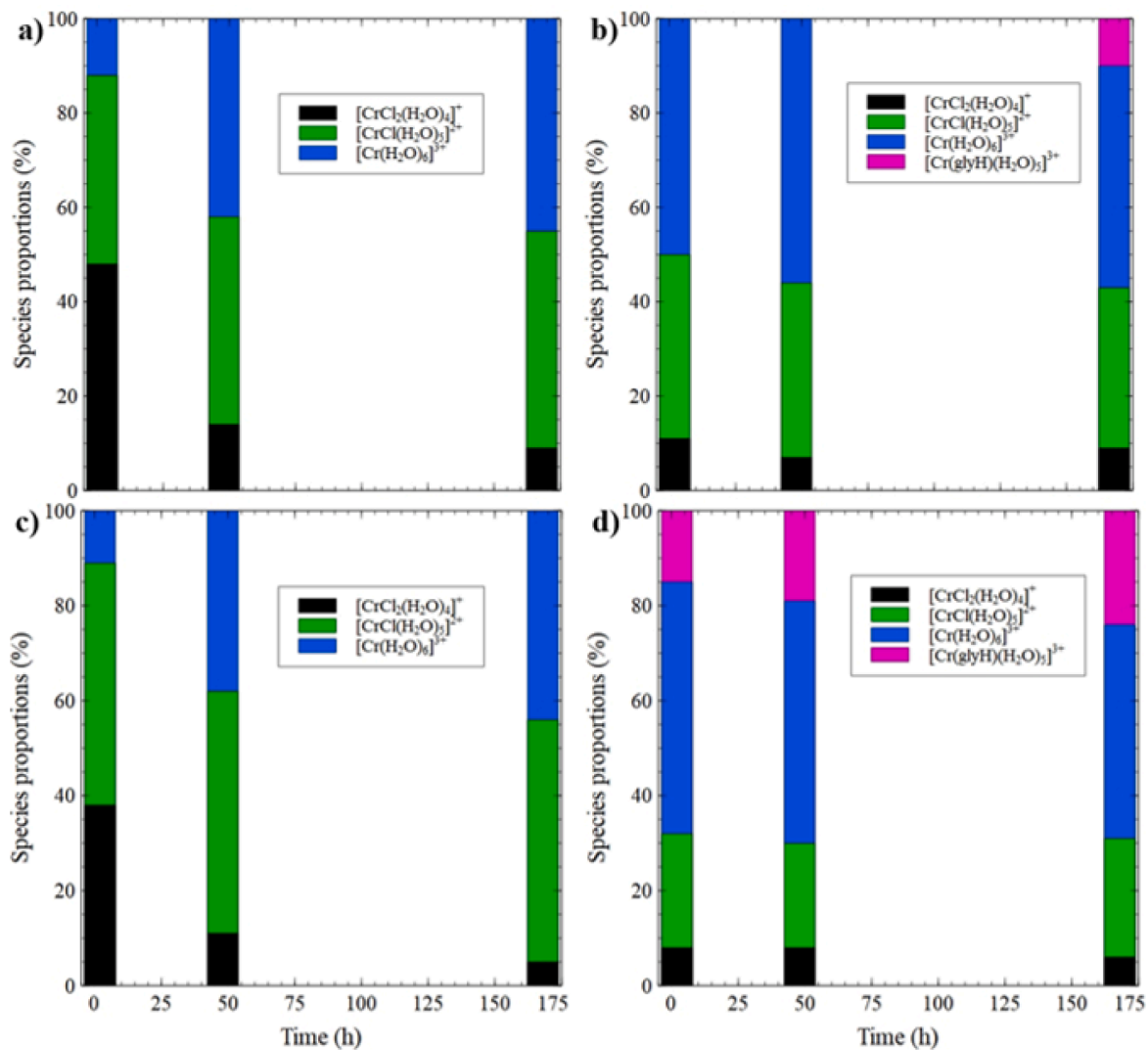


Fig. 9. Proportions over time of complexes present at pH < 2 in 1:1 electrolyte not heated (a), heated 1 h at 80 °C (b); 1:0.25 electrolyte not heated (c), heated 1 h at 80 °C (d).

Capillary electrophoresis revealed three peaks in correlation with the addition of glycine: one due to free glycine and two others likely related to chromium glycine complexes — $[\text{Cr}(\text{glyH})(\text{H}_2\text{O})_5]^{3+}$ and $[\text{Cr}(\text{glyH})_2(\text{H}_2\text{O})_4]^{3+}$. As expected, a decrease in the chromium concentration enhanced chromium-glycine complex formation, to the detriment of hexaaquachromium complex compared to a 1:1 ratio.

Overall, these UV–visible spectrophotometry and capillary electrophoresis analyses showed no chromium-glycine complex for pH lower than 2, which is the regular condition for electrodeposition. Only a higher Gly:Cr ratio and/or a pH higher than 2.4 (i.e. $\text{pK}_{\text{a}1}$ of glycine) allowed glycine-complexes to be observed in the solution. As these conditions could be met during electrodeposition near the substrate/electrolyte interface, it is highly likely that chromium depletion together with the pH increase that occurs could favor the formation of glycine-complexes at the interface, which are reported as being required to achieve homogeneous chromium deposits.

CRedit authorship contribution statement

Ariane Dasque: Investigation, Writing - original draft, Writing - review & editing. **Marie Gressier:** Writing - review & editing. **Pierre-Louis Taberna:** Writing - review & editing. **Marie-Joëlle Menu:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rechem.2021.100207>.

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