Comparative Spectroscopic Study of Cr(III) in Water and Ionic Liquids as Electrodeposition Solvent

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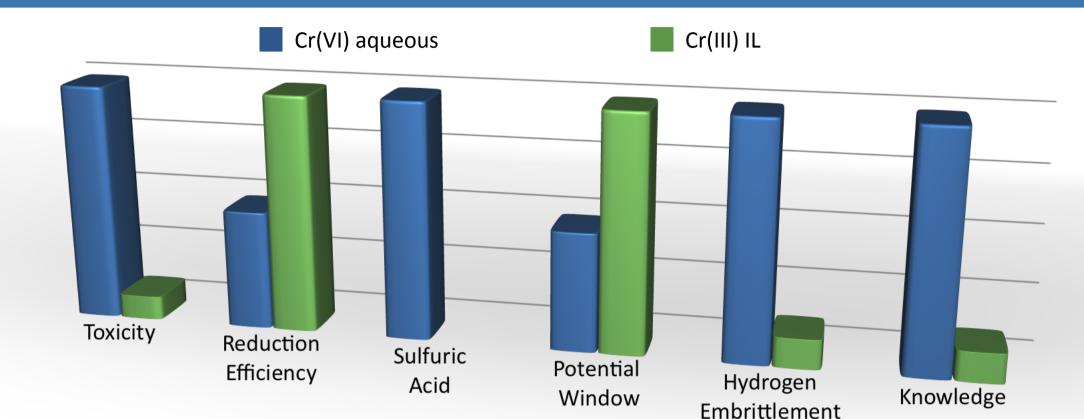
Introduction

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During the cold rolling of steel, the thickness of the steel strips is reduced by applying a high pressure with two rolling cylinders. These cylinders have to be protected from the harsh conditions. Hence, they are coated with a hard chromium layer which is typically electrodeposited from an aqueous solution containing Cr(VI). Powered by the quest to a **sustainable** production process and by the incentive of new European legislations, OCAS NV has already been working for six years on a patented Cr(VI)-free alternative. This new hard chrome-plating process is established by the electrodeposition (ED) from a **Cr(III)** containing **ionic liquid (IL)** on a steel substrate¹.

Aqueous Cr(VI) vs. Cr(III) IL ED Process¹









Research goal

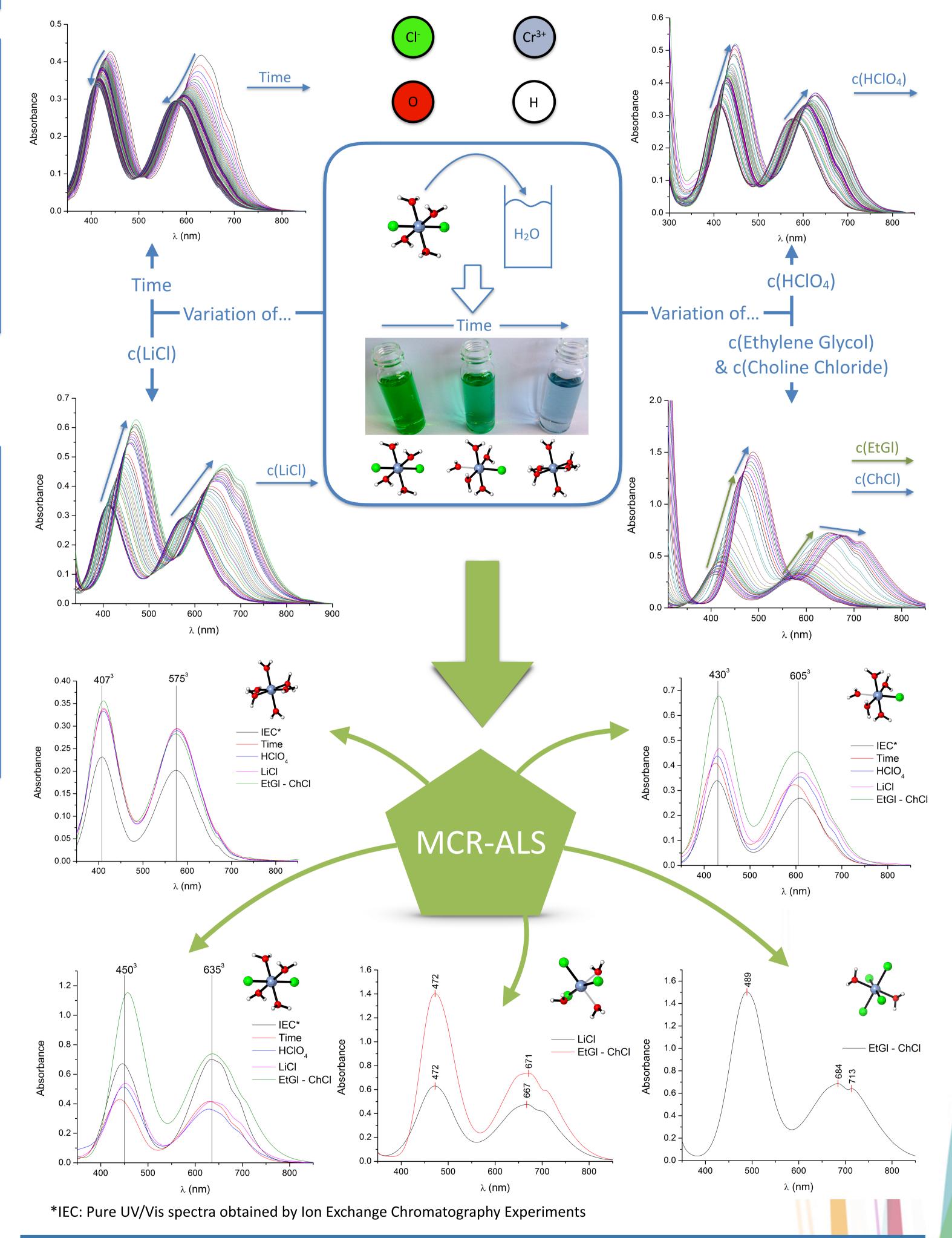
Due to the lack of fundamental knowledge of the deposition mechanism, it is far from straightforward to predict the in-use properties of the layer. Therefore, this project focuses on the elucidation of the coordination chemistry of the Cr(III) species in the IL as a function of composition and the presence of additives, and the link of this knowledge with the properties of the eventual hard chromium layer.

MCR-ALS of Cr(III) in Ethaline200

MCR-ALS

Multivariate Curve Resolution - Alternating Least Squares² is a statistical method based on Principal Component Analysis (PCA) to find the 'pure' spectra of compounds contained in a mixture. This is performed on a series of UV/Vis spectra originating from samples where the composition is slightly varied. Hence a continuous variation in peak position and intensity can be observed (Fig. 1a). Five different **chromium(III)** species where found (Fig. 1b), which each have a concentration profile along series of spectra (Fig. 1c).

Overview of MCR-ALS Results



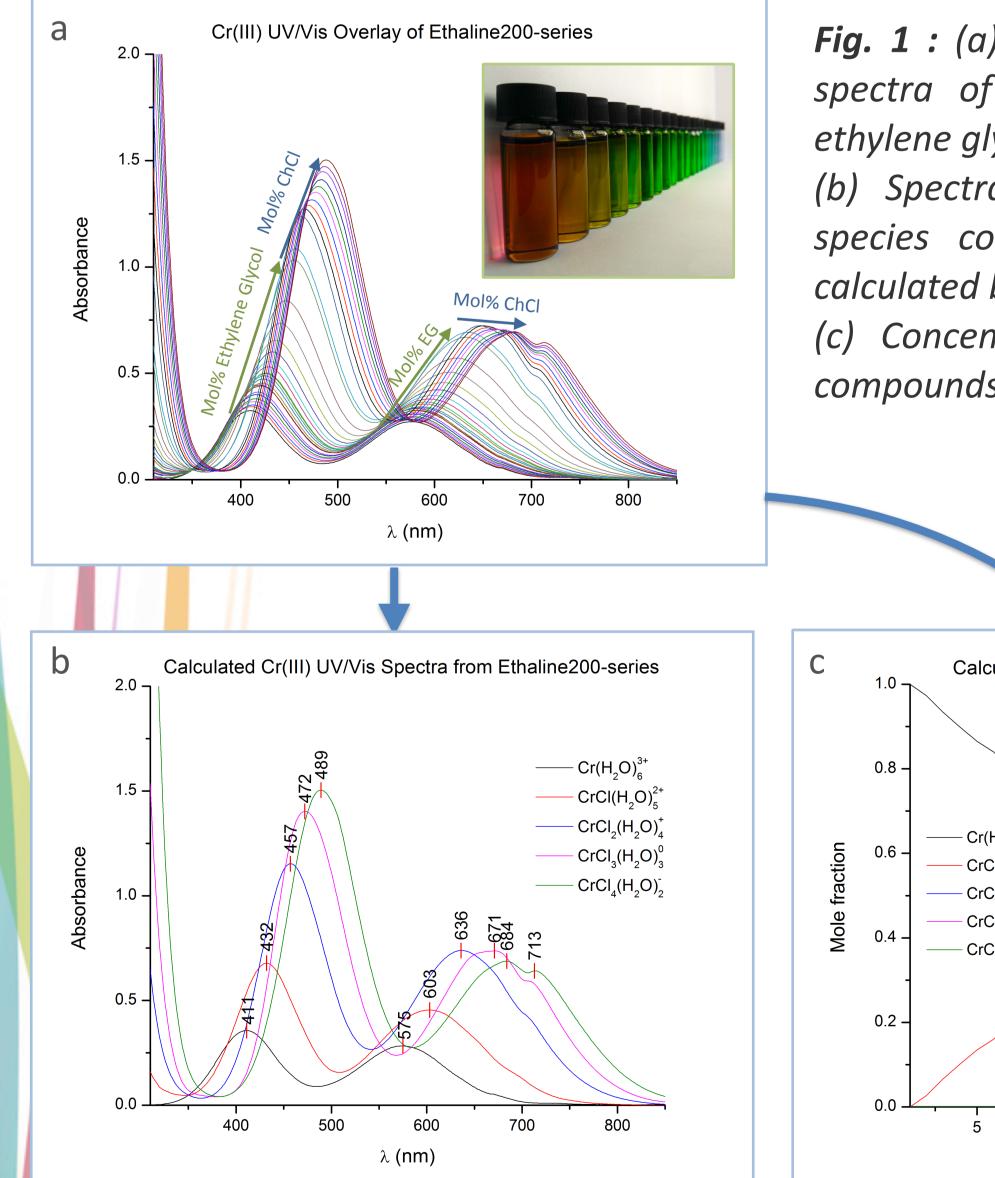
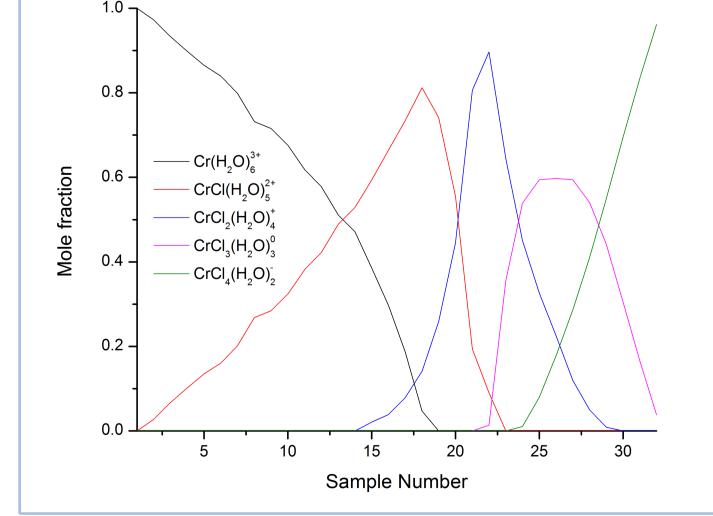


Fig. 1 : (a) Series of UV/Vis absorption spectra of 0.02 M Cr(III) in water ethylene glycol - Ethaline200. (b) Spectra of the five chromium(III) species contained in the IL mixture, calculated by MCR-ALS analysis. (c) Concentration profiles of the five compounds.

Calculated Conc. Profiles from Ethaline200-series



Semi-industrial Pilot Line



Fig. 2: Due to the promising features of this

References

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- 2. Jaumot, J., de Juan, A. & Tauler, R. MCR-ALS GUI 2.0: New features and applications. Chemom. Intell. Lab. Syst. 140, 1–12 (2015).
- 3. Elving, P. J. & Zemel, B. Absorption in the Ultraviolet and Visible Regions of Chloroaquochromium(III) lons in Acid Media. J. Am. Chem. Soc. 79, 1281–1285 (1957).



Conclusion

new electrodeposition solvent, a flexible semiindustrial pilot plant has been designed in OCAS NV. In this way, several set-ups, IL compositions, additives, etc. can be tested and evaluated on a large scale, and compared with lab scale experiments.

The pure UV-Vis spectra of five chloro-aquachromium(III) species where unraveled by means of MCR-ALS analysis in both Ethaline200 and aqueous solutions. These results were compared with results obtained by ion exchange chromatography and literature data³ to assign the different coordination compounds to the calculated spectra. These data can be used to study the ratio of the species in a large range of solvents, including ILs.