

CHAPTER 6 CONCLUSIONS

In this chapter we will show how the research objectives stated in Chapter 1, were achieved. To facilitate this discussion a summary of the research aims and objectives will be provided prior conclusions of each Chapter or section.

6.1 Design of Flow-Through Cells and Development of Methodology to Correct for IR Voltage Drop Using an Open Cell.

The flow-through cells were successfully designed using different geometries to suit different applications. PEEK material was used for development of these cells since there was no negative influence of solvents used in this study on this material in a long term. Calibration of these flow-through cells using ferrocene was effective. High concentration of background electrolyte solution was recommended for minimizing the resistance. Since IR voltage drop depends on metal charges, it was found that IR cannot be the same for different compounds even if they were measured at the same experimental conditions.

6.2 Testing of the Three Flow-Through Cells.

The designed flow-through cells were tested using ferrocene as an electroactive species by varying the flow rate and scan rate during CV experiments.

- With all the three flow cells it was possible to choose the experimental conditions that favour convection/diffusion-controlled (polarogram-shaped) or diffusion-controlled (peak-shaped) voltammograms.
- With the flow-by electrochemical cell 1, processes were not controlled purely by convection, i.e. at slow scan rates of 50 mV/s and high flow rates of 1.52 ml/min; they were controlled by mixed mode (convection and diffusion). At slow scan rates of 50 mV/s and low flow rates of 0.46 ml/min, processes were controlled only by diffusion and result were very much similar to those obtained in the bulk solution in an open cell. Flow-by cell was by far more versatile as it can be used for fundamental, mechanistic, speciation, quantitative and qualitative studies performed on-line.

- With wall-jet cells all processes were controlled purely by convection at slow scan rates. Processes controlled by mixed-mode (convection and diffusion) were only achieved at high scan rates (~ 200 mV/s and above) and low flow rate (0.46 ml/min). A wall-jet cell was recommended for quantitative analysis as it generated a significantly higher analytical signal.
- On-line mixing proved to be a very convenient method to be used in quantitative analysis as one could prepare solutions of different concentrations on-line. This resulted in a linear relationship between peak current and concentration after IR voltage drop correction. A linear relationship was not achieved before IR voltage drop correction since the anodic peak potential shifted to more positive potentials with increase in analyte concentration. IR voltage drop correction played a major role since it resulted in anodic potentials which are independent of the analyte concentrations. It follows that one should redesign the cells to bring the reference electrode much closer to the working electrode to minimize IR drop and this can be achieved when using flow-by cell.

6.3 Electrochemical Behaviour of $\text{CoCl}_2(\text{PPh}_3)_2$ in a Mixture of Acetonitrile and Pentanol (1:1)

- Investigation of the influence of a kind of working electrode material used on recorded voltammograms.
 - Pt electrode demonstrated an electrochemical activity at E_p values above 1.2 V in this solvent mixture, which was attributed to oxygen evolution which arisen because there were traces of water present in background solvents leading to formation of PtO at the electrode surface.
 - GC showed no electrochemical activity in this solvent mixture at a studied potential range (from 0 to + 1.8 V). However, the activity of the GC WE could not be maintained for more than a few cycles in solutions containing $\text{CoCl}_2(\text{PPh}_3)_2$, CoCl_2 and TEACl. GC appeared to be an excellent WE to use for electrochemical studies in non-aqueous solutions containing traces of water since it had the largest available potential window in comparison to Pt WE. GC electrode appeared to be an excellent electrode for studying compounds in non-aqueous solutions containing water, as it gave a flat or small background current,

but because of the chloride present in the studied compounds it was difficult (or impossible) to study these compounds using this electrode. Moreover, GC WE can be recommended for monitoring of compounds that do not oxidize it, for example PPh_3 .

- Gold electrode gave rise to an irreversible oxidation peak at $E_p = 1.20$ V in the solvent mixture, so it was immediately ruled out as a possible electrode material.
- Among the three electrodes investigated above, we decided to use Pt since it gave well-defined oxidation peaks of the complex, $\text{CoCl}_2(\text{PPh}_3)_2$ even in the presence of moisture in the solvents. Moisture could not be eliminated entirely from the system since we a simple distillation procedure was used for distillation of solvents and the curves were recorded in batch solutions open to air and moisture.
- Identification of the electrode processes observed from the voltammograms.
 - Cyclic Voltammetry indicated that the complex $\text{Co}^{\text{II}}\text{Cl}_2(\text{PPh}_3)_2$ can be oxidized into three different forms or stages, the first oxidation potential involving a metal oxidation Co^{II} to Co^{III} , and was followed by a chloride ligand oxidation at $E_p = 0.95$ V which was complicated by a catalytic reaction occurring after the electrode reaction causing a considerable diffusion current enhancement at $E_p = 1.40$ V.
 - Chloride is capable of binding to $\text{CoCl}(\text{PPh}_3)_3$ resulting in replacement of one PPh_3 ligand by a chloride ligand forming $\text{CoCl}_2(\text{PPh}_3)_2$. No further replacement of PPh_3 by chloride could occur which suggested that the complex $\text{CoCl}_2(\text{PPh}_3)_2$ was the most stable. This was seen from appearance of a new chloride oxidation peak at less positive potentials after addition of excess chloride.
 - CV showed that addition of excess PPh_3 resulted in depletion of chloride ions away from the WE surface leading to formation of an autocatalytic reaction. Addition of 30 equivalent concentration of PPh_3 resulted in appearance of an irreversible oxidation peak of free PPh_3 . UV-Vis and ^{31}P NMR spectroscopy did not provide us with any further information since the absorption peaks of $\text{CoCl}_2(\text{PPh}_3)_2$ and that of PPh_3 were observed at almost the same position.
 - Chronoamperometry showed that one-electron is involved during oxidation of Co^{II} to Co^{III} (oxidation peak 1) and another one-electrons is involved during oxidation of a chloride ligand (peak 2) from the complex $\text{CoCl}_2(\text{PPh}_3)_2$.

- Ferrocene as a possible internal standard to be used during electrochemical measurements.
 - Use of ferrocene as an internal standard for compounds containing chloride cannot be recommended since ferrocene oxidized chloride ion. One will have to choose other compounds like substituted ferrocene that can be used as internal standards that are inert to side reactions.
- Determine a diffusion coefficient of ferrocene in a mixture of acetonitrile and pentanol (1:1).
 - The value of diffusion coefficient of ferrocene was found to be 2.12×10^{-5} cm²/s.