E2-22: Electrocatalytic reduction of chloroacetic acid

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The extensive use of agrochemicals and fertilizers in Sri Lanka has been a risk to the environment. Among commonly used agrochemicals organochlorine compounds have a higher lifetime, and therefore it is desirable to have accurate analytical techniques to detect them. The existing analytical techniques such as gas chromatography and HPLC for detection of organic pesticides have some limitations. Electroanalytical methods can overcome some of these limitations and they are precise, accurate and relatively inexpensive.

In this study, electrocatalytic reduction of chloroacetic acid is investigated using glassy carbon electrodes coated with metalloporphyrin catalysts. Chloroacetic acid is environmentally significant because its sodium salt is a common post-emergence contact herbicide that can affect a wide range of annual weeds at seedling stage. It can also be used in combination with 'atrazine' to control total weed on non-crop lands.

The compound 5,10,15,20-tetraphenylporphyrinato iron(III) chloride [Fe(III)TPPCl] and chloroacetic acid were purchased from Aldrich Chemical Company Ltd. and BDH Chemical Ltd., respectively. Dichloromethane was analytical grade and distilled prior to use. Analytical grade lithium chloride was used as the supporting electrolyte to prepare all electrolyte solutions. Freshly distilled water was the medium in all studies. Deaeration of the electrochemical cell was accomplished by spraying with nitrogen.

All cyclic voltametric experiments were performed with an Oxford Instruments potentiostat and voltamograms were recorded on a Yew Instruments Model 3022 X-Y recorder. The 3-electrode system consists of the glassy carbon (GC) working, platinum wire counter and the saturated calomel (SCE) reference electrodes.

The glassy carbon electrode was cleaned using an alumina slurry on a polishing pad for about 30 sec. The metalloporphyrin coating solution was prepared in distilled dichloromethane, and a thin film of the catalyst was introduced on the electrode surface by dipping the cleaned electrode into the coating solution.

Chloroacetic acid is not electrochemical active in aqueous medium within the working potential range of bare glassy carbon electrodes. Consequently, it is impossible to use such electrodes to investigate the presence of chloroacetic acid in aqueous solutions.

Electrodes show different electrochemical properties when they are coated with reagents. Glassy carbon electrodes coated with tetraphenylporphyrinato iron(III) chloride showed a remarkably small background current compared to that of an uncoated electrode. More interestingly, such coated electrodes

were able to reduce chloroacetic acid at a significantly lower potential (-0.23 V), indicating the catalytic behaviour of metalloporphyrins.

During this electrocatalytic process, direct reduction of iron from Fe(III) to Fe(II) state takes place in conjunction with the reduction of chloroacetic acid.

Cyclic voltametric experiments conducted at metalloporphyrin coated glassy carbon electrodes in the presence of chloroacetic acid at different scan rates indicate that the catalytic reduction process is controlled by diffusion. It was also observed that the coated electrodes used in this study have a fairly high stability on cyclic voltametric scans.

Organochlorine compounds are not electroactive within the working potential range of glassy carbon electrodes. However, tetraphenylporphyrinato iron(III) chloride behaves as an effective electrocatalyst for the reduction of chloroacetic acid, which is a commonly used herbicide. This catalytic reduction is found to be a diffusion controlled process.

Financial assistance by NARESA for research grant number RG/94/C/01 is acknowledged.