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Three Electrode Cell Assembly for Voltammetric Measurements in Non-Aqueous Solvents

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The present study describes the construction and use of three electrode cell assembly for voltammetric measurements in non-aqueous media. This cell offers several advantages like ease of handling, low volume of the sample solution, besides offering minimum junction potential.

INTRODUCTION

The application of voltammetry in the study of metal complexes[1] as well as the determination of various species in non-aqueous solvents[2] are known. Ortiz *et al.*[3] have reported the recent developments in cyclic voltammetry at the dropping mercury electrode.

The electrochemical behaviour of organic and inorganic compounds is now widely studied by voltammetric measurements (*viz.*, cyclic voltammetry and polarography). There have been a few reports on the design of suitable cells for these measurements in non-aqueous medium[4]. Even microlitre quantity of the sample solution can be analysed in these cells[5, 6]

A simple and inexpensive cell, that contains not more than 10 mL of the sample solution, offers minimum junction potential, is easy to handle, facilitates quick change of sample solution, is suitable for non-aqueous solvents and holds different electrodes, has not been reported so far. The present paper describes such a cell assembly wherein these features have been incorporated.

EXPERIMENTAL

The details of the major features of the three-electrode cell assembly are presented in Fig. 1. The entire cell assembly is made of corning glass. A small inlet (not shown in the figure) is provided at the top of the sample compartment to maintain a positive atmosphere of nitrogen inside the compartment. The electrical contacts from the working electrode and auxiliary electrode are made via mercury in the former case and by direct contact in the latter case. In the case of platinum electrode, the surface area of the electrode is 1 cm × 1 cm. When a hanging mercury drop electrode is used, the surface area of the electrode varies with the drop size. However, in polarographic measurements the drop size from DME is maintained constant throughout the experiment by keeping the level of mercury in the reservoir at constant height from the top of the capillary. The pool of mercury can be conveniently changed along with the sample solution by making use of a stopper at the bottom of the sample compartment.

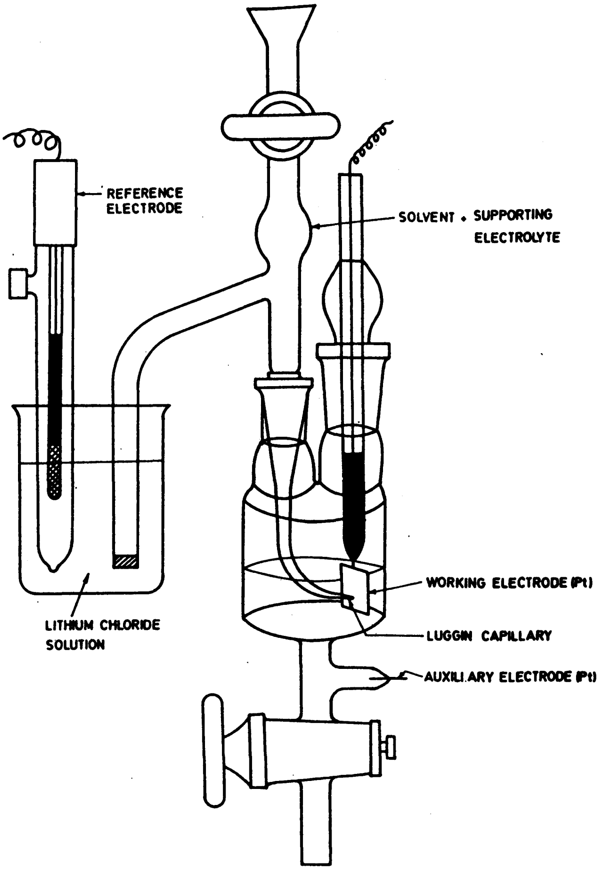

Fig. 1. Electrochemical Cell for Voltammetric Study in Non-Aqueous Solvents

A G_4-sintered glass disc is used to separate the bridge electrolyte in the salt bridge from the filling solution. The bulb provided at the top of the bridge helps store excess electrolyte solution, so that when the electrolyte solution at the tapered end of the luggin capillary is contaminated by the sample, it can be removed by partially opening the stopcock provided at the top of the bridge.

RESULTS AND DISCUSSION

In the case of aqueous solutions, the commonly used reference electrode (SCE) and the sample solution can be connected through an aqueous salt bridge that does not offer any resistance to the transport of solvent molecules across the junction. However, in non-aqueous solutions the liquid junction potential arising between two different solvent junctions can be greatly reduced by the appropriate choice of the bridge solvent and the electrolyte. The bridge solvent should have minimum interaction with either of the solvent it connects and the mutual heats of solution should be very low. The transport numbers of cation and anion of the bridge electrolyte should be close to 0.5 at all concentrations, or else the chemical incompatibility between the cell electrolyte and the salt bridge may render the emf measurements highly problematic. The only satisfactory way of minimizing this effect would be the use of the same solvent and electrolyte in the sample solution and in the bridge.

Since the cell current flows through the salt bridge, the resistance of the salt bridge should be kept as low as possible to minimize IR drop. For voltammetric work, a larger junction area is needed to obtain low resistance, which can be accomplished by the use of a glass frit. The glass frit also prevents the entry of foreign solution and trace contaminants from the filling solution. The tapered end of the luggin capillary is kept as close to the working electrode as possible.

The choice of electrolyte solution in the compartment that connects one end of the salt bridge and the reference electrode is also important. The use of KCl is not recommended as it tends to clog the pores of the glass frit due to its limited solubility in many aprotic solvents like DMF, DMSO, etc., thereby resulting in an erratic junction potential. This difficulty can be overcome by the use of LiCl solution, which has higher solubility in these solvents.

The reference electrode such as Ag/AgCl is a better choice in the cells without liquid junction. The calomel electrode is widely used because it is reproducible, stable and possesses many of the characteristics of the ideal reference electrode when it is used at a particular temperature[7].

The voltammetric cell described in the present study (Fig. 1) comprises a compartment that holds the cell solution and the auxiliary platinum electrode. The reference electrode (SCE) is connected through a salt bridge containing the supporting electrolyte [tetraalkyl ammonium salt (0.1 M)] and the non-aqueous solvent used for the study. The working electrode can be either a hanging mercury drop electrode or Pt-disk. In both the cases the luggin capillary is very close to the electrode surface. The provision of the stop-cock with stoper at the bottom of the cell facilitates the easy removal of the sample solution and the solvent used for cleaning the cell. This arrangement reduces the time required in changing the sample solutions after clearing the cell. The small volume of the sample solution (8–10 mL) required for the study in this assembly enables one to make use of lesser quantity of the sample and the solvent. The same assembly is also used in polarographic studies wherein DME is used as the working electrode. The junction potential is also kept minimum because of the reasons detailed in earlier paragraphs. The cyclic voltammogram of a macrocyclic cobalt(II) complex in DMF medium using tetraethyl ammonium perchlorate (TEAP) as the supporting electrolyte on a PAR170/173/175 system has been reproduced (Fig. 2).

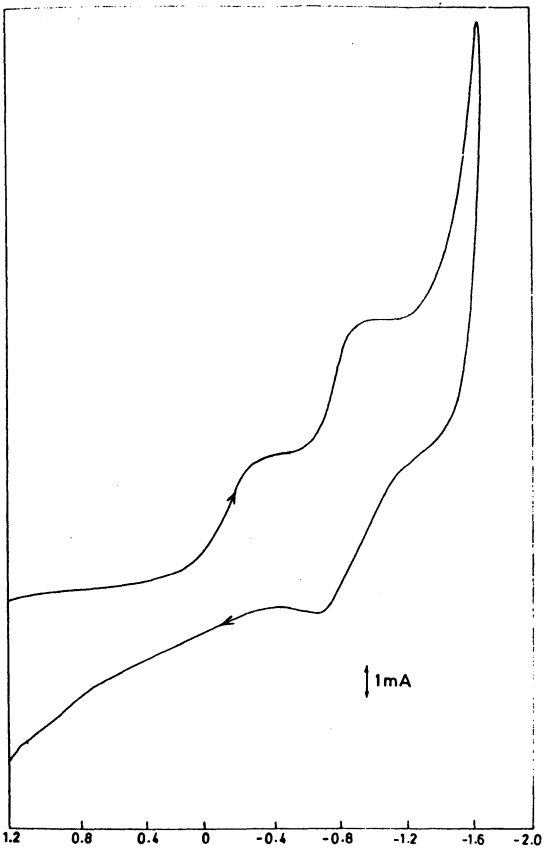

Fig. 2. Cyclic Voltammogram of [Co(BG–tn)OH] ClO_4 in DMF/TEAP. Scan rate = 100 mV/sec

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