E2-30: Concentration of electrolytes and solvent effects voltammetry

N Priyantha, A Bandara
(Dept of Chemistry, Univ of Peradeniya)

The shape and the location of voltammetric peaks depend on the concentration of the supporting electrolyte and on the composition of the solvent system, if mixed solvents are used. Preliminary experiments should be conducted to optimize these parameters before an analytical experiment. However 0.1 M supporting electrolyte solutions are usually used for electrochemical measurements, without any prior optimization. Further, mixed solvent systems are rarely used in electrochemical studies.

Cyclic voltammetric studies of catechol at bare glassy carbon electrodes in aqueous lithium chloride electrolyte solutions of concentrations varying from 0.001 M to 0.100 M showed a variation of peak currents and peak separations. The highest cathodic and anodic peak currents for the catechol/catechol quinone system were observed at an electrolyte concentration below 0.1 M. However, the peak separation increased with decreasing electrolyte concentration, indicating the expected deviation from reversibility.

The effect of the composition of the solvent on peak current and peak potential is complicated. Cyclic voltammetric studies in the water/acetonitrile mixed solvent system with compositions varying from 100% water to 05% H_2O:95% CH_3CN for the same analyte and the electrolyte indicated that the reversibility of the catechol/catechol quinone system was improved as the acetonitrile percentage increased. No systematic variation in peak currents and peak separations was observed during the change in the acetonitrile content in the medium.