E2-24: Electrochemistry of some common redox systems on polyaniline electrode

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Redox properties and electrode kinetics of some common redox systems such as $Fe(CN)_6^{3-}(aq)$, $Fe(CN)_6^{4-}(aq)$; Q(aq), $QH_2(aq)$ (where Q stands for quinone) and $I^-(aq)$, $I_2(aq)$ on polyaniline electrode surface are described.

Cyclic voltammograms (CVs) of all these systems were recorded from deoxygenated solutions containing 0.1 dm^{-3} $NaClO_4$ at pH 2. All systems hada common feature of one reduction peak and one oxidation peak although the peak positions were found to be different for different systems. Peak positions of a given system were scan rate dependent.

The first two systems, i.e., $Fe(CN_6)^{3-}(aq)$, $Fe(CN)_6^{4-}(aq)$, $NaClO_4(aq)$,/ Polyaniline and Q(aq), $QH_2(aq)$, $NaClO_4(aq)$/ Polyaniline had the folowing features in their CVs:

(i) Peak current increased with $\nu^{1/2}$ but not proportional to it (where ν is the scan rate);

(ii) Peak separation ΔE_p was greater than 59/n mV and increased with increasing ν where n is the number of electrons transferred;

(iii) I_p^A/I_p^C was equal to unity; where A and C stand for anodic and cathodic respectively;

(iv) E_p^C shifted negatively with increasing ν

These features clearly showed that the redox mechanism of both these systems on polyaniline surface was quasi-reversible.

The electrochemistry of the system, $I^-(aq)$, $I_2(aq)$, $NaClO_4(aq)$/ Polyaniline was different from that of the other two systems. This system did not satisfy conditions for reversible, quasi-reversible or irreversible electron transfer mechanisms. The following features were extracted from its CV

(i) I_p^A/I_p^C < 1 but tends to unity as ν increases ;

(ii) $I_p^C/\nu^{1/2}$ decreased slightly with increasing ν ;

(iii) E_p^C was more positive than that for reversible electron transfer ;

(iv) E_p^C shifted negatively with increasing ν

These features suggest that this redox system obeyed ec mechanism. Therefore, the electron transfer was followed by a chemical reaction.