Abstract:

Homarine and trigonelline are reduced at the carboxylic acid group at mercury electrodes in acidic solutions. In dc polarography and cyclic voltammetry, reduction yields the hydrated aldehyde, but controlled-potential electrolysis at a stirred-mercury pool electrode proceeds to the pyridinium alcohol. An ECEC—DISP mechanism for reduction of the carboxylic acid group to hydrated aldehyde is proposed. Such a mechanism involving homogeneous chemical reactions was clearly demonstrated for homarine, which probably exists in an associated form in the bulk of solution. An ECEC—DISP mechanism is also probable for trigonelline, although the reaction involves adsorption. Nonlinear regression analysis allowed deconvolution of an adsorption prewave severely overlapped with the diffusion wave. The limiting surface concentration ($3.1 \times 10{-}10$ mol cm−2) indicated that each adsorbed molecule occupies 0.54 nm2. Comparison with areas calculated for different molecular orientations suggested that trigonelline is adsorbed with the pyridinium ring parallel to the surface of the electrode.