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Diffusion-Controlled Irreversible Reduction of 2-Amino-4,6-dimethyl-5-(4′-sulphonamoyl) azopyrimidines: Integrated DC Polarographic and Cyclic Voltammetric Evidence

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Abstract: *The electrochemical reduction of 2-amino-4,6-dimethyl-5-(4'-sulphonamoyl)azopyrimidines was studied at a dropping mercury electrode (DME) and glassy carbon (GC) electrode in Britton–Robinson buffers (pH 2.0–12.0) using DC polarography, cyclic voltammetry (CV), and controlled potential electrolysis (CPE). Four derivatives were examined: R = guanylsulphonamoyl, methyloxazolylsulphonamoyl, pyrimidinylsulphonamoyl, and 4,6-dimethylpyrimidinylsulphonamoyl.*

The linearity of diffusion current (id) with √h and concentration (C), and peak current (ip) with v^1/2 and C, confirmed diffusion-controlled behavior at all pH values. The absence of anodic peaks in CV, combined with peak potential (Ep) shifts of 58–73 mV per decade of scan rate and logarithmic slopes of 0.092–0.141 V per decade, along with Tomes criterion ($E_{3/4} - E_{1/4}$ = 100–115 mV), established the irreversible nature12 of the electrode process.

Transfer coefficient values (αna) ranged from 0.35–0.51 (from Ep shift) and 0.42–0.64 (from logarithmic analysis). Diffusion coefficients (D) were calculated as 0.50–4.3 × 10^{-6} cm^2 s^{-1} using Ilkovic and Randles–Ševčík equations. Standard heterogeneous rate constants (k^0f,h) were in the range 8.0 × 10^{-7} to 6.8 × 10^{-5} cm s^{-1}, with ψ < 0.2, confirming irreversibility.

CPE results indicated a two-electron reduction (n = 2.00 ± 0.05) leading to hydrazo products. At pH values above pK (7.2–7.7), micellar effects reduced D by 3.9–5.6 times; however, diffusion control persisted. The reduction mechanism involves $2e^-$,$1H^+$ below pK and $2e^-$,$0H^+$ above pK.

Keywords: dropping mercury electrode