ADDITIVE CYCLIC SQUARE WAVE VOLTAMMETRY FOR ADSORPTIVE COMPLEX CATALYTICAL IRREVERSIBLE SYSTEM

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In this paper, the current and peak potential equations of Additive Cyclic Square Wave Voltammetry for adsorptive complex catalytical irreversible system were reported.

For equilibrium constant of complexing reaction \( K < < 1 \), the current is controlled by the rate of complexing reaction and the equation is:

\[
ic{A}(j) = nFA(DoKC_L C_q k_s C_z)\frac{1}{2}taC_m^*[X(j) + X(j + 1) + X(4H + 1 - j) + X(4H + 2 - j)]
\]

where \( X(j) = k_{j+1}^+ / k_j C_z \)^\frac{1}{2} + \sum_{j=1}^{\tau} \exp[\tau \cdot T(j)] \exp[ - \tau \cdot T(j)] .

\[
T(j) = \sum_{j=1}^{\tau} K_j
\]

The peak potential equation is:

\[
E_{p} = E^0 + \frac{RT}{nF} \ln \frac{2K_s RT}{anF \Delta E} + INT(\frac{E_s - 5\Delta E}{2\Delta E}) \Delta E
\]

For \( K > > 1 \), the current is not controlled by the rate of complexing reaction, equations of additive cyclic current and peak potential are:

\[
ic{A}(j) = nFA(Do k_\text{acc} C_z)\frac{1}{2} C_m^*[X(j) + X(j + 1) + X(4H + 2 - j)]
\]

\[
E_{p} = E^0 + \frac{RT}{anF} \ln \frac{2K_a RT}{anF \Delta E} + INT(\frac{E_s - 7\Delta E}{2\Delta E}) \Delta E
\]

It is shown that \( \text{i}_{cA} \) is proportional to \( ta \) and \( C_m^* \) \( \frac{1}{2} \) for \( K < < 1 \) but proportional to \( \frac{1}{2} \) and independent of complexant concentration for \( K > > 1 \). Therefore, we could decide which type of reaction (\( K < < 1 \) or \( K > > 1 \)) in the adsorptive complex catalytical irreversible system being occurred. However, other properties of \( \text{i}_{cA} \) for \( K < < 1 \) and \( K > > 1 \) are quite similar. For example, current curve is asymmetrical, peak current is proportional to \( C_m^* \) and in linear dependence of \( C_z \frac{1}{2} \), \( \Delta E \), and \( 1 / \tau \) respectively. It is also shown that \( E_p \) moves to more positive as \( E_s \) increases. The equations are experimentally verified with Ti(IV)-PAR-H_2O_2-BrO_3^- system, experiment and theory are found to be in reasonable agreement.

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