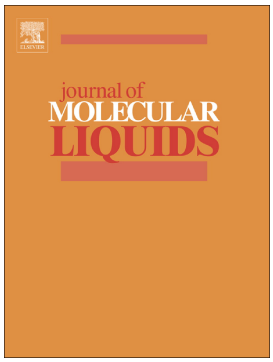

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Original Research Article

Influence of premicelles and micellar aggregates of ionic and nonionic surfactants in the oxidative decarboxylation of L-lysine by gold(III) complexes

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ABSTRACT

The influence of premicelles and micellar aggregates of the anionic surfactant sodium dodecyl sulfate (SDS) and nonionic surfactant Tween-20 in the oxidative decarboxylation of L-lysine by Au(III) complexes has been investigated spectrophotometrically at different temperatures in AcOH-NaOAc buffer medium (pH ~ 3.72-4.79). Monopositive form of lysine $(H_2A)^+$ has been found to be kinetically active reductant while two different gold(III) complexes, namely, $AuCl_4^-$ and$AuCl_3(OH)^-$ are the predominant oxidant species. Gold(III) complexes receive a nucleophilic attack by the lysine to form a transient intermediate complex which subsequently experiences a two electron redox decomposition leading to gold(I) and iminium ion in the rate determining step. Iminium ion readily undergoes hydrolysis to produce 5-aminopentanal as the principal oxidation product. Before CMC, in case of Tween 20, the premicellar aggregates bring the reactants in close proximity through H-bonding and enhance the reaction rate. However, the premicellar aggregates of SDS with lysine restrict the entry of Au(III) species towards the amino acid reaction centre and decrease the rate sharply. The observed micellar effects on the reaction rate have been explained in terms of the association/solubilization of the reactant species into the Stern /palisade layer of the micellar pseudophase through electrostatic and H-bonding interactions. Lysine-micelle binding is moderated by the entropy change during the transfer of lysine from aqueous to micellar pseudophase and the enthalpy change for such transfer is determined by compensation between lysine-water, micelle-water and lysine-micelle interactions.

Keywords: L-lysine, Au(III) complexes, electron transfer reaction, premicelle cluster, substrate micelle binding, kinetics and mechanism.