ABSTRACT

Solvent medium plays a vital role in the rate of \([\text{Fe(CN)}_6]^{3-}\) reduction and photoreduction of two series of cobalt(III)-alkyl amine and cobalt(III)-aryl amine complexes in mixed solvents. For this, various compositions of water-methanol/1,4-dioxane (0, 5, 10, 15, 20, 25 and 30 % (v/v) organic cosolvent) binary mixtures were used. \([\text{Fe(CN)}_6]^{3-}\) reduction of cobalt(III) complexes follows second order rate, hence, the rate constant \(k_2\) as well as quantum yield value, \(\Phi_{\text{Co(II)}}\) were chosen for analysis. The reduction mechanism involves solvent sensitive ion-pairs, like \{\text{Co(III)} ; \text{Fe(II)}\} and \{\text{Co(III)} ; \text{radical}\} which are better solvated than the reactants, therefore, \(k_2/\Phi_{\text{Co(II)}}\) increases as the concentration of methanol/1,4-dioxane in the medium increases. This solvent effects influence on \(k_2/\Phi_{\text{Co(II)}}\) were analysed through Linear Free Energy Relationship, LFER, using simple as well as multiparametric approaches. In the former case, \(\log k_2/\log \Phi_{\text{Co(II)}}\) were subjected to regression analysis using parameters like \(\varepsilon_r\), (relative permittivity) and Y (Grunwald-Winstein’s solvent ionising power). The results indicate the general solvent medium participation in the formation and stability of ion-pair/radical pair responsible for an increased \(k_2/\Phi_{\text{Co(II)}}\). Secondly the data were subjected to multiparameter analysis using empirical parameters like Swain’s A and B, Krygowski-Fawcett’s \(E_T^N\) and \(D_N^N\) and Kamlet-Taft’s solvatochromic parameters \(\alpha\), \(\beta\) and \(\pi^*\) to understand microlevel solvational contributions on \(k_2/\Phi_{\text{Co(II)}}\). Lastly, the data were also subjected to solute structure effect on reactivity employing the nature of chelate/Hammett’s \(\sigma\) constant and Taft’s dual substituent parameters. This investigation establishes the quantitative estimation of solvent effect on reactivity as well as solute structure on reactivity.