

Abstract:

This work demonstrated the synthesis and voltammetric studies of imidazolidine nitroxyl free radical (LH) complexes of chromium, manganese and vanadium. Half-wave potentials of solutions containing the three metal-LH as well as the metal free ligand (LH) ranged between -0.18 and -0.20 V (vs. Ag/AgCl) for the reduction process. At a potential window ranging from -0.10 to $+1.00$ V no oxidation peak was observed for LH. However, LH accepts an electron readily, leading to both forward and reverse peaks. It is not clear whether the added electron pairs up with the unpaired electron on the ligand radical or possibly forms an ion radical. On the other hand Cr-LH, Mn-LH and V-LH solutions undergo oxidation within the same potential range. A value of n ranging from 0.62 to 1.2 was obtained from a plot of E_{app} versus $\log[i/i_d - i]$, which gave linear relationship for the reduction of the four solutions, suggesting fast electron transfer from the electrode to the M-LH or metal free ligand. Reduction of the three metal-ligand solutions exhibited certain degree of electrode reversibility depending on the scan rate. Absence of an anodic peak at low scan rates suggested fast electron transfer followed by a homogeneous chemical reaction (EC mechanism), which removed the oxidized species from the surface of the electrode. The pseudo-first-order rate constants for the M-LH anion radical ranged from 0.025 to 0.087 s^{-1} . Overall, k_f increased in the order: V-LH < Cr-LH < Mn-LH.