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Abstract: The transfer of electrons to the dications of viologens including methyl viologen, diquat, benzyl viologen and n-butyl viologen was studied at the surface of a platinum disk electrode. The rate constants for the processes were determined and the effects of solvent, temperature and working electrode studied. The studies showed that the rate constants increase with temperature and the effect of solvent on the heterogeneous electron transfer rate constant is related to the polarity, dielectric constant and viscosity of the solvent and on the electrode material. Theoretical rate constants were calculated by considering the effects of barrier crossing probability and nuclear-frequency factor. Optimization of the theoretical values of rate constants at different reaction sites was carried out by comparing with experimental results. Activation parameters for the process were also obtained.

Key Words: and abbreviations used k^0 Heterogeneous electron transfer rate constant k_{exp}^0

Experimental rate constant for heterogeneous electron transfer process. MV^{++} Methyl viologen dication V^{++} Viologen dication NBV^{++} n-Butyl viologen dication BV^{++} Benzyl viologen dication BQ^{++} Diquat dication k_{Th}^0 Theoretical rate constant for heterogeneous electron transfer process

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