Investigation of the influence of solvent dynamics on the electron transfer in simple organic systems using electron spin resonance spectroscopy

Patcharanan Choto\textsuperscript{1,2,}\textsuperscript{*}, Kenneth Rasmussen\textsuperscript{3}, Guenter Grampp\textsuperscript{4}

\textsuperscript{1}Center of Chemical Innovation for Sustainability (CIS), Mae Fah Luang University, Tasud, Muang, Chiang Rai 57100, Thailand
\textsuperscript{2}School of Science, Mae Fah Luang University, Tasud, Muang, Chiang Rai 57100, Thailand
\textsuperscript{3}European Space Research and Technology Centre, Keplerlaan 1, 2201 AZ Noordwijk, The Netherlands
\textsuperscript{4}Institute of physical and theoretical chemistry, Graz University of technology, Graz 8010, Austria
*E-mail: patcharanan.cho@mfu.ac.th

Abstract: The influence of multiple relaxation processes on the electron transfer reactions was studied in the well-known redox couples of TCNE/TCNE\textsuperscript{-} and DDQ/DDQ\textsuperscript{-} (TCNE = tetracyanoethylene, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone) in non-Debye solvents. Analyses of the experimental results using longitudinal relaxation times in the limits of low (\(\tau_L0\)) and high (\(\tau_L\omega\)) frequencies are compared in order to decide which of these best describes the solvent dynamic effect observed in the reactions. The rate constants of the electron self-exchange reactions at room temperature were obtained by means of ESR line broadening experiments. The results are analysed within the framework of the Marcus Theory and the characteristic reorganization energy is determined. Both systems clearly indicate an adiabatic behavior governed by the longitudinal relaxation time, \(\tau_L\) of the solvents, where the TCNE/TCNE\textsuperscript{-} system is fully adiabatic (\(\alpha = 1\)), and the DDQ/DDQ\textsuperscript{-} couple shows a small diabatic contribution to the effect (\(\alpha = 0.85\)). Furthermore, both redox couples indicate that the best results are obtained when using the high frequency limiting \(\tau_L\omega\).

Keywords: Electron transfer; Solvent dynamic effect; Adiabatic dynamics; ESR line broadening experiments