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Voltammetric and Spectroscopic Properties of the Ammonia Adduct of Pyrroloquinoline Quinone (PQQox).

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The interaction of PQQ_{ox}, pyrroloquinoline semiquinone (PQQ_{sem}), and pyrroloquinoline quinol (PQQ_{red}) with ammonia has been investigated by cyclic voltammetry, absorption spectroscopy, and electrochemical electron spin resonance spectroscopy. The voltammetric and spectroscopic measurements show that PQQ_{ox} reacts with ammonia, yielding 5-imino-PQQ_{ox}, which is reduced reversibly to 5-amino-PQQ_{red} via a 5-aminyll PQQ_{sem} radical by a two-step one-electron mechanism. Theoretical analyses of the ammonia concentration dependence of the redox potentials and the absorbance give the constants of the ammonia adduct formation of PQQ_{ox}, PQQ_{sem}, and PQQ_{red} as 6.9×10^2 , 6.5×10^2 , and $9.3 \times 10^2 \text{ M}^{-1}$, respectively, at pH 9.2.

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Electrochemical and Electron Spin Resonance Study on the Interaction between α -Cyclodextrin (α -CyD) and Electrochemically Generated Radical Intermediate of *p*-Nitrophenolate anion (NP⁻).

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The interaction between α -CyD and an electrogenerated intermediate radical (NP^{•2-}) of NP⁻ in aqueous solution has been investigated by electrochemical and *in-situ* ESR spectroscopic techniques. Fast scan cyclic voltammetry showed that α -CyD forms a 1 : 1 complex with NP^{•2-} as well as with NP⁻, the formation constant being 20 M^{-1} , and suppresses the subsequent reaction of NP^{•2-}. An ESR spectral study of NP^{•2-} provided evidence for the incorporation of NP^{•2-} into the α -CyD cavity: the addition of α -CyD suppressed the tumbling motion of NP^{•2-} and hence enhanced the anisotropic effect due to the hyperfine interaction of the ¹⁴N nucleus.

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Oxidation and Reduciton Potentials and Electron-Transfer Interaction in Photoexcited States.

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The equations on the oxidation and reduction potentials in excited state are derived, which leads to the important relation between the oxidation-reduciton potentials in ground and excited states. Also, the mutual correlation of oxidation-reduciton potentials in ¹L_a excited state to those in ground stata is discussed for a benzenoid alternant hydrocarbon. Finally the electron-transfer interaction of an electron donor and an electron acceptor has been considered in photoexcited states by virtue of oxidation-reduction potentials. The equation thus obtained is of the same type as that formulated semiempirically by Rhem and Weller. Our treatment provides theoretical background for the Rhem-Weller equation.