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Inclusion and Stabilization of Electrochemically Generated Anion Radicals of Dicyanobenzenes by Cyclodextrins in Water.

KENJI KANO*, KAZUYA MORI, BUNJI UNO, MASASHI GOTO,
TANEKAZU KUBOTA

The interaction between cyclodextrins (CyDs) and the electrogenerated-intermediate anion radicals of dicyanobenzenes in aqueous solutions has been investigated by cyclic voltammetry and in situ electrochemical ESR spectroscopy. The anion radicals of the present dicyanobenzenes are included more tightly than the parents and stabilized in a microscopic environment of the CyD cavity with respect to the consumptive homogeneous chemical reaction. The unusual stronger inclusion of the anion radicals can be explained in terms of their dipole-induced dipole interaction. The dependence of the formation constants on the dicyanobenzene isomers and the CyDs is interpreted in view of the steric specificity.

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Voltammetric and Spectroscopic Studies of Pyrroloquinoline Quinone (PQQ) Coenzyme under Neutral and Basic Conditions.

KENJI KANO*, KAZUYA MORI, BUNJI UNO, TANEKAZU KUBOTA,
TOKUJI IKEDA, MITSUGI SENDA

Voltammetric and spectroscopic properties of PQQ have been investigated in the pH range from 5 to 13.5. PQQ gives a reversible cyclic voltammogram at the mercury electrode, which has been ascribed to a two-step one-electron redox reaction of the *o*-quinone moiety. Digital simulation analysis of the reversible voltammogram made it possible to evaluate the standard redox potentials of PQQ/pyrroloquinoline semiquinone (PQQ_{sem}) and PQQ_{sem}/pyrroloquinoline quinol (PQQ_{red}) couples. From the redox potential *vs.* pH relationships, the acid dissociation constants of PQQ, PQQ_{sem}, and PQQ_{red} have been determined. The adsorption and ESR spectroscopic properties are explained by the acid-base and redox equilibria proposed here.

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Voltammetric Determination of Acid Dissociation Constants of Pyrroloquinoline Quinone (PQQ_{ox}) and Its Reduced Form (PQQ_{red}) under Acidic Conditions.

KENJI KANO*, KAZUYA MORI, BUNJI UNO, TANEKAZU KUBOTA,
TOKUJI IKEDA, MITUGI SENDA

The Voltammetric properties of the coenzyme PQQ_{ox} have been investigated in the pH range from 0 to 8. PQQ_{ox} gives a quasi-reversible cyclic voltammogram at a platinum electrode, which is ascribed to a two-electron redox reaction of PQQ_{ox} to the quinol type PQQ_{red}. From the analysis of the standard redox potential (E°) *vs.* pH relationship, the four macroscopic acid dissociation constants (K_a) of both PQQ_{ox} and PQQ_{red} have been determined. The E° of the PQQ_{ox}/PQQ_{red} couple at pH 7.0 has been determined as -0.175 V *vs.* SCE (a saturated calomel electrode) with a semiquinone (PQQ_{sem}) formation constant of 0.02.