STABILITY OF SUBSTITUTED ARYL GROUPS ELECTROCHEMICALLY GRAFTED ON CARBON ELECTRODES.

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Carbon (eg. glassy carbon) electrodes have been recently functionalized with 4-substituted phenyl groups by electrochemical reduction of the corresponding phenyl diazonium tetrafluoroborate salt dissolved with an appropriate electrolyte in acetonitrile. The functionalization involves the reaction of an aryl radical with the carbon surface (1, 2). This may lead to the formation of close packed monolayers of substituted aryl groups. However, the radical mechanism can yield secondary reactions and three-dimensional growth of polymer structures consisting of aniline groups linked to one another (3).

In the present work, phenyl groups with substituents such as 4-carboxy, 4-nitro, 4-diethylamine (DEA) and 4-bromo were grafted at glassy carbon electrode surface. The stability of these grafted groups was studied at various electrode potentials in aqueous media. In appropriate experimental conditions, the as-grafted groups severely inhibit the cyclic voltammetry response of selected redox probes. Thus, the reappearance (and/or increase) of an electrochemical response, after polarization, was taken as an indication that a modification of the grafted layer occurred. Our results demonstrated that polarization at very positive (ca. 1.8 V) and negative (ca. -2 V) potentials are needed to observe an electrochemical response. Electrochemical impedance spectroscopy was also used to investigate the stability of the grafted layers and our results indicate that the impedance data usually tracks fairly well with the cyclic voltammetry results.

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