

Electrochemical behavior of DNA in carbon paste electrodes modified with hydrophilic and hydrophobic natural deep eutectic solvents (NADES)

Beatriz A. Fernandes (PG)^{1*}, Rafael M. Buoro (PQ)¹.

beatrizall1@usp.br;

¹ Departamento de Química e Física Molecular, Instituto de Química de São Carlos- Universidade de São Paulo

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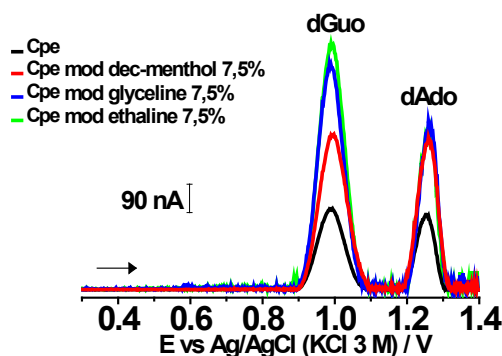
Highlights

Carbon paste electrodes were modified with hydrophilic and hydrophobic natural deep eutectic solvents. The hydrophilic NADES modified electrodes presented higher current nucleoside oxidation peaks.

Abstract

Carbon paste electrodes with different modifier binders have been studied to develop DNA-based sensors that allow the quantitative determination and study of the interaction mechanism of DNA with small molecules. Natural deep eutectic solvent (NADES) is an alternative class of electrode carbon paste modifiers, considered a class of green solvents generally composed of a hydrogen-bond acceptor (HBA) and a hydrogen bond donor (HBD) [1]. Understanding the redox behavior of the DNA in novel binders is critical for the design and successful application of the sensor. In this work, it was investigated the electrochemical behavior of DNA at paste carbon electrodes modified with hydrophilic (ethaline and glyceline) and hydrophobic (dec-menthol) NADES (CPE NADES) using cyclic (CV) and differential pulse voltammetry (DPV). The used NADES were prepared by mixing HBA and HBD in a specific molar ratio under stirring and controlled temperature (60 °C) until the formation of a homogeneous liquid [2]. The CPEs NADES modified-DNA were prepared by successively covering the electrode surface with three drops each of 10 µL from a 50 µg mL⁻¹ dsDNA [3]. The DPV voltammograms showed two well-defined peaks corresponding to deoxyguanosine (dGuo) oxidation, at $E_{pa} = +1,05$ V, and deoxyadenosine (dAdo), respectively at $E_{pa} = +1,3$ V as previously stated in literature, but with increased currents for the NADES modified binders. Adding NADES to the binders reduces the intrinsic hydrophobicity of the mineral oil, as choline chloride is a positively charged ammonium quaternary salt. Therefore, the dsDNA negatively charged phosphate backbone interacts with the electrode surface through electrostatic interactions extending the dsDNA and leaving the nitrogenous bases more available to be oxidized. Thus, this study showed that the NADES can be used with binders in CPES for developing DNA-based sensors with increased sensitivity and evinced that the electrochemical behavior of dsDNA and current intensity of dGuo and dAdo depends on the binder hydrophilicity. The ethaline modified carbon paste electrode with 7,5% presented as the best substitution percentage with superior electroanalytical performance and was selected for the preparation of carbon paste DNA- modified for future studies of the interaction mechanism of DNA with small molecules.

Figure 1. DP voltammogram baseline-corrected in 0.1 M acetate buffer solution pH 4.5 of 50 µg mL⁻¹ dsDNA.



Acknowledgments

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