Ionic liquids for enzymatic sensing

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Introduction:

• Point-of-care (POC) glucose biosensors play an important role in the management of blood sugar levels in patients with diabetes.
• One of the most commonly used enzymes in glucose biosensors is Glucose Oxidase (GOx).
• Ionic liquids (ILs) have evolved as a new type of solvent for biocatalysis, mainly due to their unique and tunable physical properties.[1]
• Amperometric biosensors employing IL’s have been reported previously, for example, [(C₆mIm)[BF₄]] has been used as a mediator in an electrochemical H₂O₂ biosensor.[2]
• This work investigates colorimetric and electrochemical methods of glucose detection by Combining the enzyme’s specificity, with the unique characteristics of IL’s and either a chemogen (o-Dianisidine) or electrochemical mediator (ferrocene) to enhance the detection.
• This interest is driven by the need to find molecular environments in which enzymes are highly stabilized while retaining reduct activity.

Experimental:

• Ionic liquids used in this study include [C₆mIm][EtSO₄], [P₄,₆,₆,₁₄][Cl], [P₄,₆,₆,₁₄][dca] and [P₄,₆,₆,₁₄][NTf₂] (Fig 1).

Fig 1: Cations / anions used in this study.

Colorimetric:

• The mechanism of the GOx / peroxidase reaction is shown in Fig 2 for colorimetric analysis. Glucose is quantified via the indirect oxidation of o-Dianisidine.

Fig 2: Glucose quantification measured using colorimetric analysis.

Electrochemical:

• Counter & working electrode consisted of Carbon Cloth- Graphitized Span Yarn Carbon Fabrics
• 500 µm threads consisting of a bundle of 10 µm fibres.
• Allows for flexible substrates.
• Potentials were against a Ag/AgCl reference electrode – 500 µm silver wire chloridised in FeCl₃.
• Single threads were soaked in a IL / Ferrocene / GOx enzyme solution
• The electrochemical mechanism for glucose detection in a Ferrocene mediated system[3]:

GOx-FAD+ + Glucose → GOx-FADH₂ + Glucuronolactone
2Fe⁺ → GOx-FADH₂ → 2Fe²⁺ + GOx-FAD
2Fe²⁺ → 2Fe³⁺ + 2e⁻
[electrode surface]

Results & Discussion:

Colorimetric:

• [(C₆mIm)[EtSO₄]] showed favourable results for colorimetric analysis (Fig 3).
• Varying concentrations of glucose in (C₆mIm)[EtSO₄] resulted in a linear standard curve (Fig 4).

Fig 3: Colorimetric assay for GOx in different ILs at 0.55 M glucose.

Electrochemical:

• SEM image (Fig 5) shows excellent coverage of the threads resulting in a large working surface area. Using the Anson equation, the calculated working area was approx 0.138 cm².
• Due to the hydrophobic nature of the cloth, [P₄,₆,₆,₁₄][dca] was chosen as the electrolyte.
• Significant response shown at 7.5 mM glucose addition (Fig 6).

Fig 4: Standard curve of GOx assay with [C₆mIm][EtSO₄] & varying glucose concentrations.

Fig 5: SEM images of carbon cloth & carbon cloth soaked in [P₄,₆,₆,₁₄][dca] / Ferrocene / GOx.

Fig 6: CV of Glucose additions to [P₄,₆,₆,₁₄][dca]/Ferrocene/GOx on carbon cloth. Scan rate 0.01 V/S

Conclusions:

• [(C₆mIm)[EtSO₄]] showed favourable results for colorimetric analysis (Fig 3).
• Carbon cloth shows potential as a flexible working electrode.
• [P₄,₆,₆,₁₄][dca] as an electrolyte in the glucose system shows favourable limit of detection
• A flexible, wearable one shot sensor maybe produced using IL formulations

References