

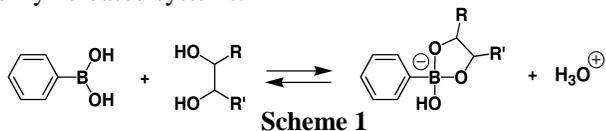
Polyaniline as A Non-enzymatic Sugar Sensor: Potentiometric Sensors Based on the Inductive Effect on the pK_a

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Sensor applications based on conjugated polymers continue to be the subject of intense research.¹ In this approach, binding of an analyte results in physical distortions or changes in electron density thereby altering conductivity.¹ Poly(aniline),² in particular, has received a great deal of attention due to its proton coupled redox chemistry and its resulting pH dependant properties. For example, poly(aniline) has been used as a pH electrode³ and has been coupled to reactions that generate or consume protons to create sensors.⁴ We will report a new strategy that exploits the inductive effect of reactive substituents on the pK_a of poly(aniline) to produce active sensing elements.

Specifically, we have focused on the complexation of diols with boronic acid⁵ since: 1) the reaction results in a change in the electron donating ability of the substituent,⁶ 2) it is reversible; and 3) glucose sensing with this approach has several advantages in comparison with enzyme-based systems.^{7,8,9}



Since enzyme-based glucose sensors are inherently sensitive to factors that influence either enzyme activity or glucose mass transport, boronic acid-based sensors provide an attractive alternative due to the fact that the complexation is a reversible, equilibrium-based reaction (*i.e.*, the analyte is not consumed). Since the redox chemistry of poly(anilines) involves both electrons and protons, the open circuit voltage, E_{oc} , is sensitive to changes in pH,^{3,4} and it follows that E_{oc} will also be a function of K_a and in turn any changes in electron donating ability of substituent groups.

The inherent selectivity of the boronic acid complexation reaction (Scheme 1) to the nature of the diol is illustrated in Figure 1 by the change in the E_{oc} upon the addition of the same concentrations of different sugars. The difference in sensitivity qualitatively follows the difference in binding constants with phenylboronic acid reported in neutral aqueous solutions (fructose > glucose¹⁰ > α -methyl-D-glucoside).

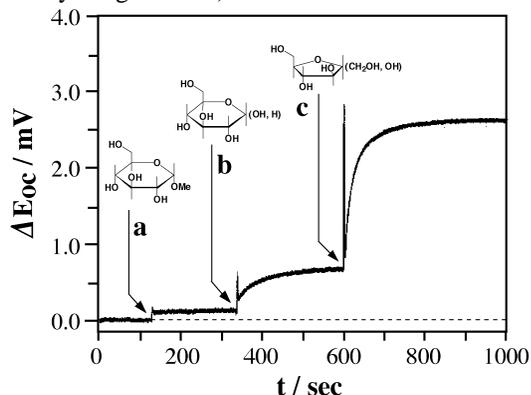


Figure 1. Response curve of a poly(aniline boronic acid) electrode as a function of time upon addition of 6.8 mM: a) α -Methyl-D-glucoside; b) D-glucose; and c) fructose in pH 7.4 PBS.

A stepwise increase in E_{oc} was observed upon addition of glucose. A control experiment using only **1** exhibited similar increases in E_{oc} , however, the total shift of the potential was clearly smaller. Reversibility of the sensor was confirmed by the return of the E_{oc} to its initial value upon exposure to blank PBS.

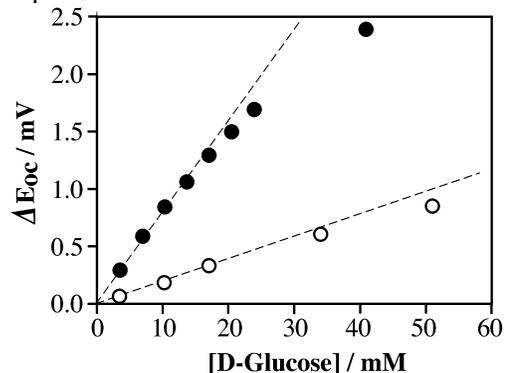


Figure 2. Calibration curves of D-glucose (filled circles) for a poly(aniline boronic acid) electrode and of D-glucose (open circles) for poly(aniline) coated electrode in pH 7.4 PBS.

In summary, we report a novel sensing approach exploiting inductive effects on the pK_a of poly(aniline) and in turn its electrochemical potential. This strategy was demonstrated using boronic acid chemistry to produce a non-enzymatic glucose sensor. The selectivity of the boronic acid complexation reaction toward different sugars was reflected in the sensitivity of the E_{oc} to various sugars. Finally, calibration curves for D-glucose obtained in PBS (pH 7.4) demonstrate that reversible responses can be obtained within the physiological relevant range 4 – 6 mM using this approach. Research into the use of this strategy with other systems is currently underway.

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