

Selective Fluoride Recognition with Ferroceneboronic Acid

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Redox active ferroceneboronic acid **1** has excellent selectivity in the electrochemical recognition of fluoride ions in the presence of other halides and common anions.

Recognition and transduction of atomic and molecular species by synthetic molecular receptors are the focus of many research groups. Neutral and ionic synthetic molecular species are known to complex common anionic species with some selectivity.^{1,2} Recent reports by Beer *et al.* and other research groups have shown that metallocenium derivatives are useful in anionic recognition in nonaqueous media.³ Meanwhile, the sp² hybridized trigonal boron atom is known to interact with certain anions and the hybrid orbital changes from sp² to sp³.⁴ In particular, the boron atom which acts as a 'hard acid' strongly interacts with F⁻ which acts as a 'hard base'. This specific boron-F⁻ interaction can stabilize the boronic acid-saccharide [S(OH)₂] complexes by changing sp²-hybridized RBO₂S to sp³-hybridized RFB-O₂S and facilitate saccharide transport across a liquid membrane.⁵ Aromatic boronic acids are also known to interact with both chlorides and fluorides in solid matrices and organic solutions.⁶ We here present our rationale towards electrochemical detection of fluoride ions in aqueous media. F⁻ Recognition is very difficult because of the strongly hydrated nature of F⁻. This has been overcome by the use of boronic acids which have a particular affinity with F⁻. In the ferroceneboronic acid, the F⁻-binding site is intramolecularly connected to a redox-active ferrocene moiety. Hence, one can read out the F⁻-binding event occurring at the boronic acid site through the shift of the redox potential of the ferrocene moiety.

Ferroceneboronic acid **1** is redox active and stable in methanol-water mixtures and in water at neutral pH. The redox

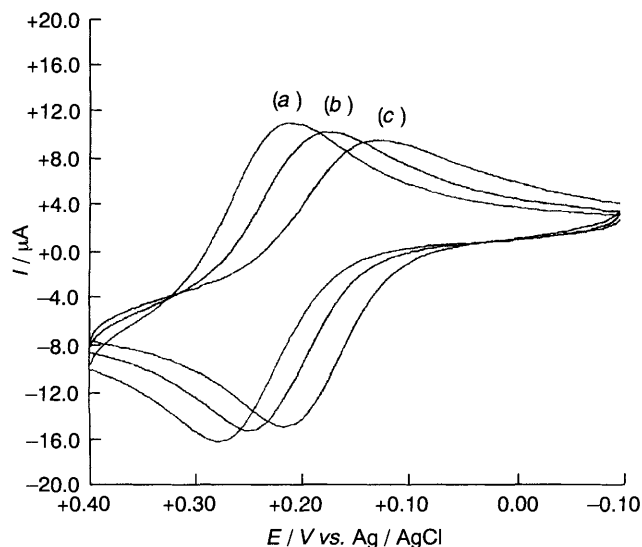
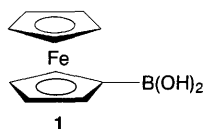
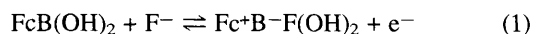


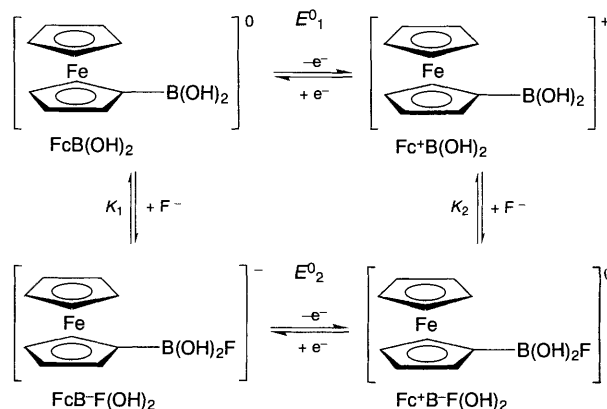
Fig. 1 Cyclic voltammograms of ferroceneboronic acid at a glassy carbon electrode [0.5 mmol dm⁻³ FcB(OH)₂, 0.1 mol dm⁻³ NaClO₄], with varying concentrations of fluoride ions, $\nu = 500$ mV s⁻¹; (a) [F⁻] = 0; (b) [F⁻] = 9.1×10^{-3} mol dm⁻³; (c) [F⁻] = 4.5×10^{-2} mol dm⁻³

properties of **1** are remarkably changed upon addition of fluoride ions into the solution (Fig. 1). The measurements were carried out in aqueous solutions at 25 °C and the electrochemical potentials were determined by cyclic voltammetry. A glassy carbon electrode was used as a working electrode and a Ag/AgCl electrode was used as a reference electrode.

The strongly electron-withdrawing nature of the ferrocenium moiety creates an electron-deficient boron centre; hence, a better interaction with fluoride ions is expected. The oxidized species of ferroceneboronic acid has a stronger interaction with fluoride ions compared to the neutral boronic acid, the main redox reaction is expressed by eqn. (1).



The stability constants, K_2 (for the ferrocenium derivatives complexation), are given in Table 1. The polarographic half-wave potential of **1** was changed upon addition of fluoride ions (as KF); no such effect was found for chloride and bromide ions even at very high concentrations. The result establishes that fluoride recognition is not affected by the presence of high concentrations of halides (Fig. 2). Sulfate ions gave a small but



Scheme 1 Most important redox active species during the electrochemical measurements assuming that thermodynamic equilibrium exists

Table 1 Complexation constants for different anions^a

Anion	$K_2/\text{dm}^3 \text{ mol}^{-1}$
F ⁻	1000 ± 50 (MeOH/H ₂ O = 1 : 9) 700 ± 50 (H ₂ O)
Cl ⁻	< 2
Br ⁻	< 2
SCN ⁻	2 ± 1
SO ₄ ²⁻	20 ± 10
H ₂ PO ₄ ⁻	10 ± 10

^a Because the curve for fluoride ions (Fig. 2) is over a range of 200 mV linear, $K_2 > 3 \times 10^3 K_1$ [$\log(K_2/K_1) > 0.2/(\ln 10 RT/F) = 3.5$]. The difference between the complexation constants (K_1, K_2) makes it possible to determine [F⁻] electrochemically. The potential change in the linear part can then be described as:

$$E = E^0_1 + RT/F \ln \left(\frac{[\text{Fc}^+\text{B}^-\text{F(OH)}_2]}{[\text{FcB(OH)}_2]} \right) - RT/F \ln (K_2[\text{F}^-])$$

for the redox reaction [eqn. (1)].^{7,8} The small K_2 values of the anions (not F⁻) are difficult to determine because the high concentrations of the salts in the electrolyte influences by itself the potentials of the electrodes.

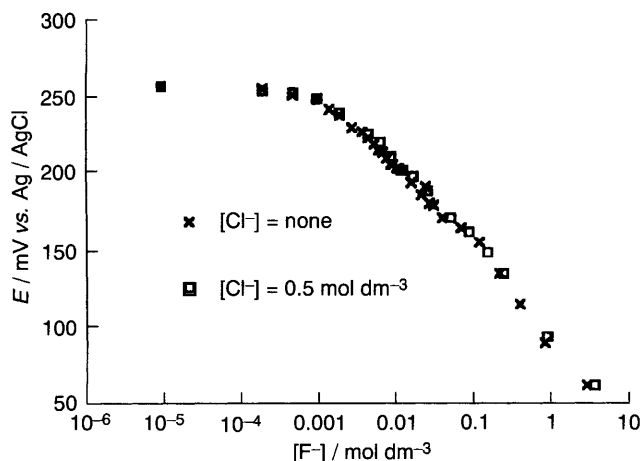


Fig. 2 Polarographic half-wave potentials of ferroceneboronic acid (5×10^{-4} mol dm⁻³ in a H₂O–methanol 9 : 1 mixture, 0.1 mol dm⁻³ NaClO₄) as a function of the concentration of fluoride ions with and without the presence of chloride ions ([Cl⁻] = 0.5 mol dm⁻³, no supporting electrolyte salt)

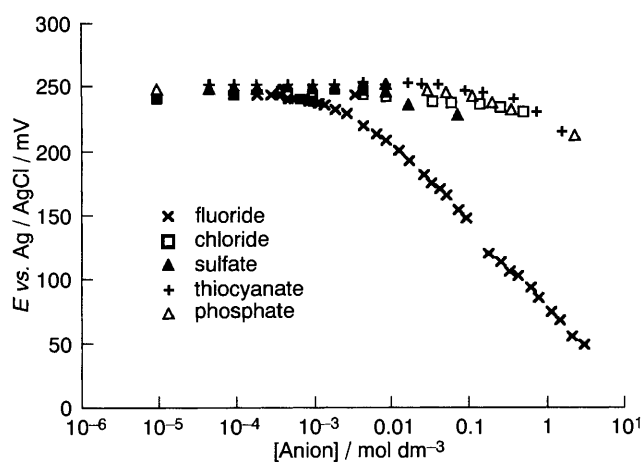


Fig. 3 Polarographic half-wave potentials of ferroceneboronic acid (5×10^{-4} mol dm⁻³ in H₂O, 0.1 mol dm⁻³ NaClO₄) as a function of the concentration of F⁻, Cl⁻, SCN⁻, H₂PO₄⁻ and SO₄²⁻

detectable change at high concentration ($K_2 = 20$ dm³ mol⁻¹) but the effect is much smaller than that of F⁻ and mostly negligible under the potential measurement conditions.

The complexation constant of the oxidized ferroceneboronic acid (K_2) is stronger in methanol–water mixture (1 : 9 v/v) than in pure aqueous solution. The polarographic half-wave potential is 250 mV vs. Ag/AgCl (Fig. 3). This potential increases with the increase in the methanol concentration.

These results show that ferroceneboronic acid is highly useful in selective recognition of fluoride ions. Chloride ions have virtually no effect on the electrode potential, nor do thiocyanate,

phosphate, sulfate and others. The complexation is caused by the strong Lewis acid–Lewis base interaction. Hydroxide ions react similarly to F⁻ with the boronic acid; but it occurs only in strongly alkaline solutions and another concurrent redox reaction occurs in parallel. The ferroceneboronic acid has similar excellent selectivity as ion selective electrodes based on LaF₃, but the principle is different.^{9†} Ferroceneboronic acid may find also industrial applications as an inexpensive and highly F⁻-selective sensor for fluoride ions (e.g. as PVC coatings on a graphite electrode).¹⁰

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Footnote

† The LaF₃ electrode is a membrane electrode containing single crystals of LaF₃, whereas ferroceneboronic acid is a redox electrode, in which mixtures of the oxidized and the neutral ferroceneboronic acid have their own stable and defined potential, controllable by the F⁻ concentration. This is one of the few examples of an organic redox electrode like a quinone/hydroquinone electrode.⁸ Based on this idea it should be possible to construct a very simple, robust and inexpensive system to determine [F⁻] for industrial applications. The redox potential of the ferroceneboronic acid can be altered by substituting the ferrocene moiety. Additionally, the properties of the boronic acid centre may be modified to create sensors for other molecules.

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