



## Mini review

## Using voltammetry to measure hydrogen-bonding interactions in non-aqueous solvents: A mini-review

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## ABSTRACT

This review briefly details some quantitative and qualitative methods to measure the hydrogen bonding abilities of electroactive and electroinactive compounds through voltammetry and provides examples of several systems that have been examined.

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## 1. Introduction

Hydrogen bonds form one of the most important intermolecular interactions by virtue of their ubiquitous nature, strength, selectivity and directionality. In recent years, there has been a growing use of electrochemistry, specifically cyclic voltammetry, to modulate and measure hydrogen-bonding interactions [1]. This is essentially due to the substantial amount of electrostatic character present in the

hydrogen bond that makes it susceptible to electrochemical perturbation. Generally, the higher the charge of an ion, the stronger the resulting hydrogen bonds will be.

One advantage of using voltammetry for detecting and characterizing hydrogen-bonding interactions is that it only requires one component of the donor–acceptor pair to be electroactive. In addition, it is not necessary for the site of the hydrogen bond to be an integral part of the redox system, but merely close enough to exert an inductive or mesomeric effect. The voltammetric technique is applicable to both diamagnetic and paramagnetic compounds, unlike NMR spectroscopy; and is not overwhelmed by a large excess of hydroxyl groups, as would be the case for infrared and <sup>1</sup>H NMR spectroscopy. Voltammetry

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has shown to be much more sensitive than UV–visible spectroscopy towards hydrogen-bonding interactions [2] and also in good agreement with results obtained from theoretical calculations [3–6].

There are, however, at least four important criteria to satisfy before the hydrogen bond system can be studied by electrochemistry. First, either the donor and/or acceptor must be electroactive. Second, their oxidized and reduced forms should be chemically long-lived under the experimental conditions and the electron transfer kinetics being reasonably fast. Third, the redox couple must be able to significantly influence the binding between the donor and acceptor. And last, the effects of proton-transfer can be differentiated from those of hydrogen bonding. A characteristic feature of hydrogen bonding is that it does not alter the chemical reversibility of the redox process, which may occur for proton-transfer reactions. This last criterion is deemed the least important since the acidity and basicity of a compound can be modified through its substituents.

## 2. Voltammetric methods for characterizing the hydrogen-bonded complex

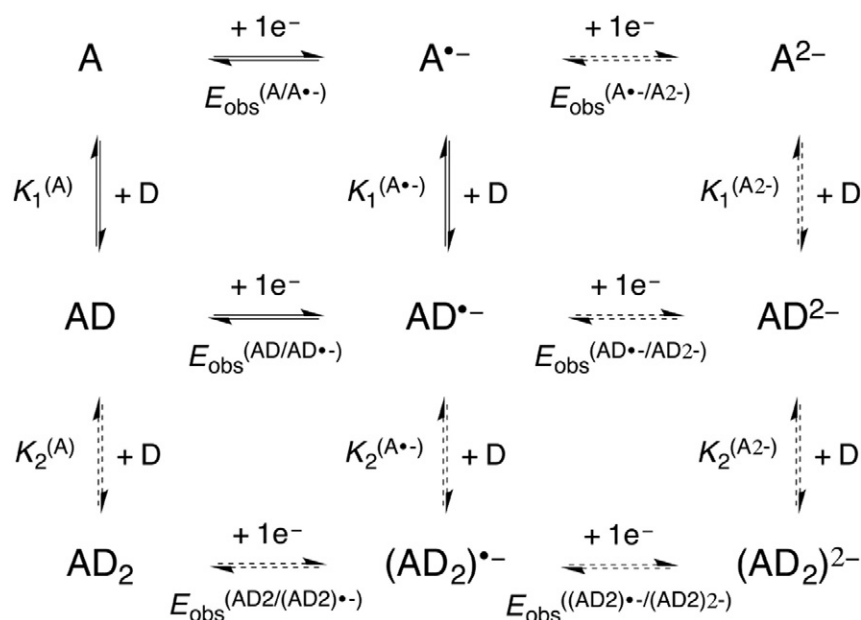
Cyclic voltammetry is the most popular electrochemical technique employed because it readily divulges qualitative and quantitative information about the hydrogen-bonded complex through the peak current,  $i_p$ , and observed potential,  $E_{\text{obs}}$ , of the redox couple. Consider the electrochemical reduction “square scheme” mechanism (in solid arrows) sketched in Scheme 1 that is often used to describe the series of electron transfers (drawn horizontally) and hydrogen-bonding interactions (given vertically) between a pair of electroactive hydrogen-acceptor (A) and electroinactive hydrogen-donor (D). An analogous reaction scheme is often applied for proton-coupled electron transfer (PCET) reactions. Similar conclusions can also be drawn in the other cases where an oxidation reaction occurs instead, where the hydrogen-donor is electroactive ( $D_{\text{act}}$ ) and the hydrogen-acceptor is electroinactive ( $A_{\text{inact}}$ ). Although this square scheme (in solid arrows) is drawn to include a one-electron transfer reaction and interactions with only one D molecule, it can be further extended both horizontally to include more electron-transfer reactions and vertically for more association reactions (as shown in dashed arrows).  $E_{\text{obs}}^{(A/A^{\bullet-})}$  and  $E_{\text{obs}}^{(AD/AD^{\bullet-})}$  are the observed half-wave ( $E_{1/2}$ ) or peak potentials of the  $A/A^{\bullet-}$  and the

hydrogen-bonded  $AD/AD^{\bullet-}$  redox couples, respectively; while  $K_1^{(A)}$  and  $K_1^{(A^{\bullet-})}$  correspondingly represent the association constants of one molecule of D to A and  $A^{\bullet-}$ . Similar representations are also used for the other members in the scheme.

The existence of hydrogen bonds between A and D may be qualitatively revealed through changes to  $i_p$  in the absence and presence of D because the measured current is partially dependent on the diffusion coefficient of the incoming redox-active species [3,7]. Hence, the formation of AD should lead to a smaller  $i_p$  because of its larger volume than unbound A.  $i_p$  is also dependent on the viscosity of the solution, which changes likewise in the absence and presence of D, and the electrochemical reversibility of the electron-transfer reaction. Therefore, quantitative analysis of  $K_1^{(A)}$  based on differences in diffusion coefficients may be more accurately achieved through chronoamperometry under purely diffusion-limited conditions.

The hydrogen-bonding efficiency of the oxidized and reduced forms of the acceptor (A and  $A^{\bullet-}$ , respectively) to the donor molecule can also be qualitatively obtained by monitoring the change to  $E_{\text{obs}}^{(A/A^{\bullet-})}$  in the presence and absence of D. If D has stronger binding to the oxidized form A then it will require more energy to reduce AD than A, and  $E_{\text{obs}}^{(AD/AD^{\bullet-})}$  will be negative of  $E_{\text{obs}}^{(A/A^{\bullet-})}$  (where  $E_{\text{obs}}^{(AD/AD^{\bullet-})}$  and  $E_{\text{obs}}^{(A/A^{\bullet-})}$  are the corresponding standard electrode potentials of the  $AD/AD^{\bullet-}$  and  $A/A^{\bullet-}$  redox couples). Hence,  $E_{\text{obs}}^{(A/A^{\bullet-})}$  will shift to more negative potentials in the presence of D. Conversely,  $E_{\text{obs}}^{(AD/AD^{\bullet-})}$  will be positive of  $E_{\text{obs}}^{(A/A^{\bullet-})}$  in the situation where the reduced form  $A^{\bullet-}$  has a greater tendency to interact with D because of greater stabilization. In this case,  $E_{\text{obs}}^{(A/A^{\bullet-})}$  will shift to more positive potentials in the presence of D.

The shifts in potential associated with hydrogen-bonding interactions can be quantitatively described by treatment of the equilibrium expressions of the Nernst equation. It can be shown through Eq. (1) that a four-membered square scheme will behave as a one-electron redox couple with  $E_{\text{obs}}$  dependent on the true values of the standard electrode potentials and association constants so long as the electron-transfer and association reactions are fast and reversible. If D is present in a large excess (i.e. D is added in more than ten times excess of A) then the concentration of unbound D may be assumed to be equal to its added concentration. And if  $K_1^{(A \text{ and } A^{\bullet-})}[D] \gg 1$  (because  $K_1^{(A \text{ and } A^{\bullet-})}$



Scheme 1. Series of electron transfers and hydrogen-bonding interactions.

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