# A Simple Method Based on NMR Spectroscopy and Ultramicroelectrode Voltammetry for the Determination of the Number of Electrons in Faradaic Processes

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*Summary: A new, convenient method to determine the number of electrons (n) involved in a faradaic process was demonstrated using a series of four compounds containing two, three, four, and eight equivalent ferrocene centers. The method takes advantage of pulse gradient stimulated echo (PGSE) NMR spectroscopy to determine the diffusion coefficient ($D_o$) of the electroactive species. The value of n is subsequently determined from the steady-state limiting current ($i_L$) measured on a disk ultramicroelectrode.*

The number of electrons (*n*) involved in an oxidation or reduction process is an important parameter that is required for the description of any oxidation or reduction process. Its electrochemical determination is typically hampered by the close association between *n* and the diffusion coefficient ($D_o$) of the electroactive species. One way to circumvent this problem is to perform full conversion electrochemical experiments, such as bulk coulometric and/or spectroelectrochemical measurements, in which the diffusion of the electroactive species plays a decreased role. However, these experiments usually require relatively specialized cells and are characterized by long time scales, which increase the likelihood of complications related to possible reactions of the electrogenerated products.[1] Several methods are available to determine *n* values using faster voltammetric experiments,[2,3] but the increasing popularity of pulse gradient stimulated echo (PGSE) NMR techniques[4] led to the development of the new and practical method described here.

Voltammetric experiments with ultramicroelectrodes (UMEs) often yield steady-state current−potential curves, as opposed to the more complicated transient responses that are usually found in similar experiments with larger working electrodes.[5] Among the various UME configurations possible, disk electrodes are often used because they are relatively easy to fabricate or commercially available. The limiting current obtained on a disk UME is given by the simple expression

$$i_L = 4nrFD_oC \qquad (1)$$

where *r* is the radius of the disk UME, *F* is Faraday's constant, *C* is the concentration of electroactive species in the bulk solution, and the remaining terms have been defined already. Given the simplicity with which $i_L$ values can be obtained from steady-state voltammograms, eq 1 affords an excellent way to determine the number of electrons involved in a faradaic process, provided that the radius of the electrode and the diffusion coefficient are obtained independently. The radius of the electrode is usually available from independent experimentation or observation with a microscope. Once a disk UME is fabricated or purchased, its radius is the subject of careful characterization. Often the nominal disk radius (obtained from the manufacturer or derived from the radius of the wire used in electrode fabrication) is verified by observation/imaging with a suitable microscope. Furthermore, the radius can be determined from experimental voltammetric data recorded with a standard electroactive species for which the *n* and $D_o$ values are known.

Bard and co-workers have described a method for the independent determination of $D_o$ values from the initial time evolution of the current measured with a disk UME under conditions of diffusion control.[6] Here, we report an alternative, simple approach that takes advantage of well-developed PGSE NMR methodology for the independent and accurate determination of diffusion coefficients. The application of PGSE NMR techniques requires a spectrometer capable of applying a magnetic field gradient along the probe's *z* axis (vertical axis of the sample tube). The application of the field gradient labels the magnetic nuclei along the *z* axis and allows monitoring of their Brownian motions. In other words, the magnetization decay as a function of time is dependent on the diffusion coefficient, which can thus be evaluated without prior knowledge of the actual concentration of the molecular or ionic species in question.[4] The fast growth in the use of PGSE techniques is a reflection of the now common field gradient capabilities in modern NMR spectrometers, but it also highlights the accuracy and convenience that this method affords to determine $D_o$ values. In this note we describe a method based on the determination of the diffusion coefficient by PGSE NMR techniques that makes possible the direct application of eq 1 to determine the number of electrons (*n*).

To demonstrate the application of the method, we selected a series of four compounds (**1**−**4**) containing two, three, four, and eight equivalent ferrocene residues in their structures (Figure 1). Compounds **1**, **3**, and **4** were either available in our group or prepared again following reported methods.[7−9] Compound **2** was prepared similarly (Supporting Information) and character-

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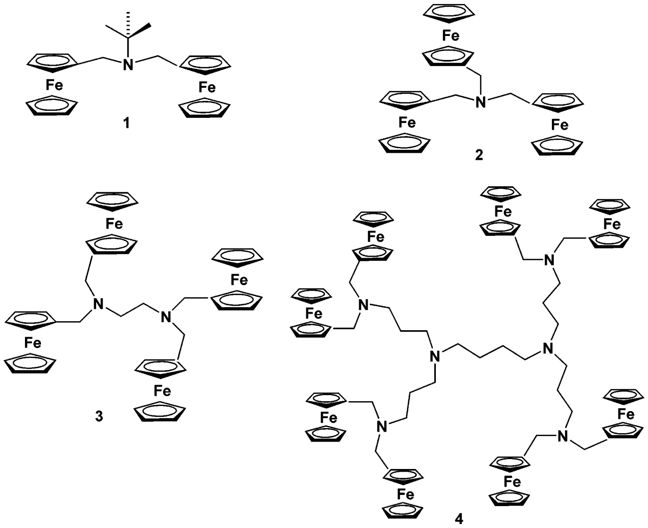

**Figure 1.** Structures of the ferrocene-containing compounds used in this work.

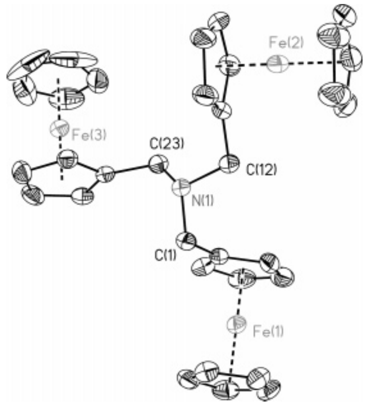

**Figure 2.** ORTEP plot of the X-ray crystal structure of **2** at the 30% probability level.

ized by $^1$H and $^{13}$C NMR spectroscopy, FAB mass spectrometry, and X-ray crystallography. Its solid-state crystal structure is shown in Figure 2. Voltammetric experiments with compounds **1**−**4** reveal the anticipated oxidation of the ferrocene groups. Compound **1** exhibits an extent of electronic communication between the ferrocene centers that is dependent on its state of protonation and solvent polarity.[7,9] Compounds **2**−**4** present a single oxidation wave, which may be broadened due to the convolution of the individual oxidation processes. In this work we will not be concerned with the mechanistic details of the oxidation of these compounds. We are simply interested in the limiting currents obtained on a disk UME when the potential is sufficiently positive to drive the electrochemical oxidation under conditions of diffusion control. As an illustrative example, the steady-state voltammetric behavior of compound **2** on a disk UME is shown in Figure 3. Similar voltammetric behavior was obtained for the four compounds surveyed, and the measured limiting currents are reported in Table 1.

PGSE NMR experiments with the series of compounds **1**−**4** yielded the diffusion coefficients ($D_o^{NMR}$) given in Table 1. The NMR spectroscopic experiments were performed at 298.5 K in $CD_3CN$ solution, with concentrations of the ferrocene-containing compounds similar to those used in the electrochemical experiments.

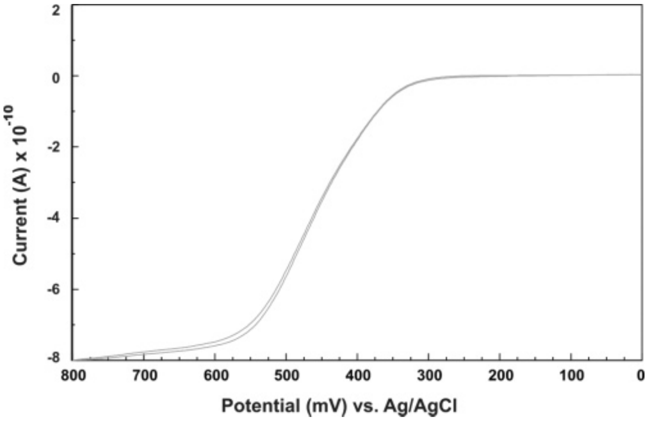

**Figure 3.** Steady-state voltammogram obtained on a carbon fiber disk UME ($r = 5$ $\mu$m) immersed in a 0.2 mM solution of **2** in $CH_3CN$ also containing 0.2 M $TBAPF_6$.

**Table 1. Half-Wave Potentials, Limiting Currents, Diffusion Coefficients, and Number of Electrons Measured for Compounds 1−4 at 25 °C**

| compd | $E_{1/2}$ (V)[a] | $10^{10} \times i_L$ (A) | $10^6 \times D_o^{NMR}$ (cm$^2$ s$^{-1}$)[b] | $n_{unc}$[b] | $10^6 \times D_o$ (cm$^2$ s$^{-1}$)[c] | $n$[c] |
|---|---|---|---|---|---|---|
| **1** | *d* | 7.15 | 8.03 | 2.25 | 8.34 | 2.16 |
| **2** | 0.54 | 8.00 | 6.60 | 3.14 | 6.86 | 3.01 |
| **3** | 0.45 | 9.20 | 5.76 | 4.18 | 5.98 | 4.01 |
| **4** | 0.50 | 14.00 | 4.57 | 7.95 | 4.74 | 7.65 |

[a] Measured vs Ag/AgCl. [b] Diffusion coefficients determined by PGSE NMR in ca. 2.0 mM solutions of $CD_3CN$ and uncorrected number of electrons. [c] Diffusion coefficients and number of electrons corrected by application of eqs 3 and 4 for viscosity and density differences between $CD_3CN$ and 0.2 M $TBAPF_6/CH_3CN$. It was found that $\eta_{CD3CN} = 0.96(\eta_{0.2MTBAPF6/CH3CN})$. [d] The two observed $E_{1/2}$ values are 0.37 and 0.48 V (see ref 9).

While the diffusion coefficients determined in the PGSE NMR experiments were obtained in $CD_3CN$ solution, the $D_o$ values required for eq 1 should correspond to a $CH_3CN$ solution also containing 0.2 M supporting electrolyte (tetrabutylammonium hexafluorophosphate, $TBA^+PF_6^-$). The difference in medium composition can be taken into account by using the Stokes−Einstein equation, which establishes that the diffusion coefficient is inversely proportional to the viscosity of the medium ($\eta$), that is,

$$D_o = kT\eta^{-1}/(6\pi r_h) \tag{2}$$

where $r_h$ is the hydrodynamic radius of the diffusing species, $k$ is Boltzmann's constant, and $T$ is the absolute temperature. Assuming that the hydrodynamic radius and temperature remain constant, we can write

$$(\mathrm{D}_o)_1\eta_1 = (D_o)_2\eta_2 \tag{3}$$

where the subscripts 1 and 2 denote the two medium compositions. The viscosities were readily measured at 25 °C by determining the flow times ($t$) of the two solutions in an Ostwald capillary viscosimeter and their densities. The solution viscosity can thus be simply calculated as

$$\eta = B\rho t \tag{4}$$

where $B$ is a calibration constant and $\rho$ is the density of the solution. Once the viscosity ratio between pure $CD_3CN$ and 0.2 M $TBAPF_6/CH_3CN$ was obtained, the $D_o$ values can be corrected for the differences in medium composition using eq 3.

The results show that the method works well. Using the uncorrected $D_o^{NMR}$ values obtained directly from the PGSE NMR experiments is not ideal because the viscosity of solutions prepared with pure deuterated solvent may differ from those prepared with the isotopically unenriched solvent plus 0.2 M supporting electrolyte. Despite this, the number of electrons ($n_{unc}$) calculated without any viscosity correction approximates the anticipated values (based on the number of ferrocene residues per molecule) and may serve as a rough approximation. After correcting the $D_o$ values for solution viscosity differences, the calculated $n$ values are satisfactory, showing acceptable error margins. Correction for solution viscosity differences has to be done only once for a particular solvent-supporting electrolyte combination. For instance, the data in Table 1 provide the correction factor from $CD_3CN$ to 0.2 M $TBPF_6/CH_3CN$ for any other electroactive species; that is, we can generally write that

$$D_o = (1.04)D_o^{NMR} \tag{5}$$

A cautionary note on the application of this method to large molecules, such as dendrimers having many identical copies of the same redox active center on their surfaces, is appropriate. Abruña and co-workers have shown that in dendrimers containing 16 or more equivalent $[Ru(bpy)_3]^{2+}$ peripheral centers the $D_o$ values extracted from cyclic voltammetric and rotating disk electrode voltammetric measurements are much lower than those obtained from PGSE NMR techniques.[10] The reason for this discrepancy is the incomplete sampling in electrochemical measurements of all the redox centers attached to a large dendrimer. Amatore and Abruña have taken advantage of this effect, using fast scan rate voltammetry to demonstrate the so-called "electrochemical microtome".[11] In this regard, we note that the negative absolute error found in the $n$ value obtained for compound **4**, which has eight equivalent ferrocene centers, might be due to incomplete redox sampling. Therefore, although we have not performed experiments with larger dendrimers, the method described here is not likely to provide accurate $n$ values for molecules exceeding the size of compound **4**.

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**Note Added after ASAP Publication.** In the version of this paper published on the Web Feb 24, 2006, an author was omitted. The author list that now appears is correct.

**Supporting Information Available:** Synthesis and X-ray crystal data of compound **2**, plus details on PGSE NMR diffusion coefficient measurements. These data are available via the Internet at http://pubs.acs.org.

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