

# The Decamethylferrocenium/Decamethylferrocene Redox Couple: A Superior Redox Standard to the Ferrocenium/Ferrocene Redox Couple for Studying Solvent Effects on the Thermodynamics of Electron Transfer

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The solvent dependence of the formal redox potentials of the ferrocenium/ferrocene ( $\text{Fc}^{+/0}$ ) and 1,2,3,4,5-pentamethylferrocenium/1,2,3,4,5-pentamethylferrocene ( $\text{Me}_5\text{Fc}^{+/0}$ ) couples versus the decamethylferrocenium/decamethylferrocene ( $\text{Me}_{10}\text{Fc}^{+/0}$ ) couple indicates that the latter is a superior redox standard for studying solvent effects on the thermodynamics of electron transfer. The couples were studied in 29 solvents and the differences in formal redox potentials between the  $\text{Me}_n\text{Fc}^{+/0}$  ( $n = 5, 10$ ) and  $\text{Fc}^{+/0}$  couples are surprisingly solvent dependent. In the case of the  $\text{Fc}^{+/0}$  couple versus the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple, the potential difference ranges from +583 mV in 2,2,2-trifluoroethanol to +293 mV in water. The positive shifts for the  $\text{Me}_5\text{Fc}^{+/0}$  couple versus the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple were about half of these values. The  $\text{Me}_{10}\text{Fc}^{+/0}$  redox couple can also be used in easily oxidized solvents, such as *N*-methylaniline and *N,N*-dimethylaniline, or in conjunction with a Hg working electrode. Statistical multiparameter analysis of the differences in potential versus empirical solvent parameters indicate that the redox potential of the  $\text{Fc}^{+/0}$  couple is more solvent dependent than that of the  $\text{Me}_5\text{Fc}^{+/0}$  couple. The latter, in turn, is notably more solvent dependent than that of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple. These results contradict the widely used “ferrocene assumption” that the redox potential of the  $\text{Fc}^{+/0}$  couple is not very solvent dependent. The data show that the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple is better suited than the  $\text{Fc}^{+/0}$  couple as a redox standard for studies of the thermodynamics of solvation of other redox couples. The data also enable previous measurements using the  $\text{Fc}^{+/0}$  couple to be corrected to values referenced against the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple.

## Introduction

As early as 1958 it was proposed that, irrespective of the nature of the solvent, the standard electrode potential of the  $\text{Fc}^{+/0}$  redox couple was invariant,<sup>1</sup> which is referred to as the “Strehlow assumption”<sup>2</sup> or the “ferrocene assumption”.<sup>3</sup> The large cyclopentadienyl ( $\text{Cp}^-$ ) ligands were assumed to insulate the change in charge of the metal center of the members of the  $\text{Fc}^{+/0}$  couple from interaction with the solvent,<sup>2,4,5</sup> and the sandwich structure of the  $\text{Fc}^{+/0}$  couple should prevent the close approach of solvent molecules to the metal center.<sup>6</sup> However, ab initio molecular orbital calculations indicate that the major change in electron density occurs on the Cp rings, since the charge on the iron atom changes only slightly on oxidation of Fc to  $\text{Fc}^+$  ( $\Delta q_{\text{Fe}} = +0.08$ ).<sup>7</sup>

In 1984, the  $\text{Fc}^{+/0}$  couple was recommended as an internal standard for reporting electrode potentials in nonaqueous solvents.<sup>8,9</sup> Internal standards are used to overcome the problem of potential variations due to changes in liquid junction potentials between the solution and the reference electrode.<sup>10</sup> In most solvents, the  $\text{Fc}^{+/0}$  couple fulfills the requirements for a suitable internal redox standard proposed by IUPAC. However, some studies showed that the chemical reversibility of the  $\text{Fc}^{+/0}$  couple in some media is incomplete because of the tendency of  $\text{Fc}^+$  ion to react with nucleophiles.<sup>11–13</sup>

While the  $\text{Fc}^{+/0}$  couple is a suitable reference for potentials measured in a single solvent, the validity of the “ferrocene

assumption” has been challenged in terms of both evidence for specific solvation effects and models of solvation.<sup>3,5,14</sup> There are several ways in which the solvent might interact with either member of the  $\text{Fc}^{+/0}$  couple and, hence, lead to a significant solvent dependence of the redox potential of the  $\text{Fc}^{+/0}$  couple. In one model, a formal redox potential,  $E_f$ , of a redox couple is considered in terms of four contributions:<sup>14</sup>

$$E_f = E_f^0 + \Delta E_p + \Delta E_H + \Delta E_s \quad (1)$$

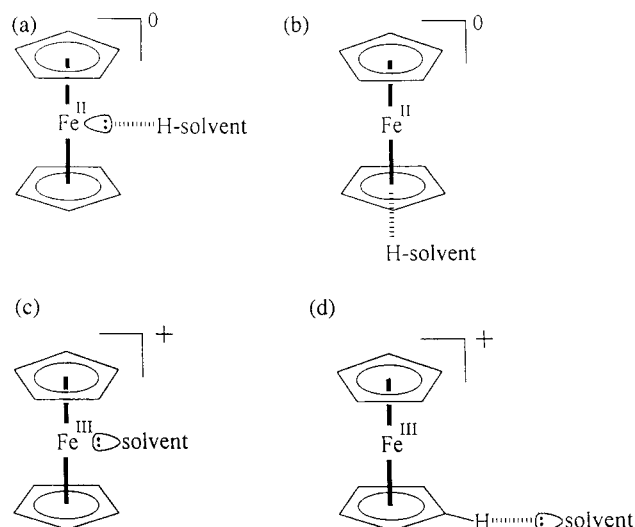
where  $E_f^0$  is the formal redox potential in the absence of all solvent interactions (akin to the ionization potential),  $\Delta E_p$  is a nonspecific term due to differences in electrostatic interactions between the solvent dipoles and the charges of the members of the couple,  $\Delta E_H$  is an interaction associated with changes in internal solvent order caused by the two oxidation states,<sup>15</sup> and  $\Delta E_s$  represents the specific solvent effects, such as solvent/solute hydrogen bonding, Lewis acid/base interactions, and solvent/solute  $\pi$ -stacking of ring systems.

One approach to delineate these solvent effects is the use of the multiparameter model of Kamlet, Abboud, and Taft,<sup>16,17</sup> which has been described<sup>18</sup> as the best empirical model of the effects of solvent on processes in solution. This model relates any physicochemical quantity to well-known solvent parameters, leading to the following expression for  $E_f$ :<sup>14,19–22</sup>

$$E_f = E_f^0 + a\alpha + b\beta + c(\pi^* + d\delta) + h\delta_H^2 \quad (2)$$

where  $\alpha$  and  $\beta$  are empirical parameters for solvent hydrogen-

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**Figure 1.** Possible interactions between the hydrogen-bonding acid and base moieties of the solvent and the members of the  $\text{Fc}^{+/0}$  couple. The oxidation state for which the interaction will be most important is indicated in the figure. The interactions indicated in (a) and (b) relate to solvent  $\alpha$  or  $A_N$  parameters, whereas those indicated in (c) and (d) relate to  $\beta$  or  $D_N$  parameters.

bonding acidity and basicity, respectively,  $\pi^*$  is a measure of solvent dipolarity,  $\delta$  is a polarizability correction term, and  $\delta_H$  (the Hildebrand solubility parameter) is a measure of solvent–solvent interactions that are interrupted in creating a cavity for the solute.<sup>15</sup> The coefficients,  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $h$ , are derived from the best fit of the experimental data. The terms in eq 1 may be equated with those in eq 2 to give

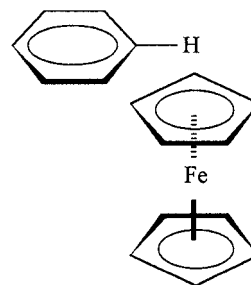
$$\Delta E_p = c(\pi^* + d\delta) \quad (3)$$

$$\Delta E_H = h\delta_H^2 \quad (4)$$

$$\Delta E_s = a\alpha + b\beta \quad (5)$$

Another model developed by Fawcett has been used in the analyses of solvent effects.<sup>23</sup> In this model, the redox potential of a redox system is correlated with acceptor number,  $A_N$ ,<sup>24</sup> donor number,  $D_N$ ,<sup>25,26</sup> polarity term,  $Y = (\epsilon_s - 1)/(\epsilon_s + 2)$ ,<sup>27</sup> and polarizability term,  $P = (n^2 - 1)/(n^2 + 2)$ ,<sup>27</sup> where  $\epsilon_s$  and  $n$  are the dielectric constant and the refractive index of the solvents, respectively.

Recent studies on the effects of solvents on the electronic state density of ferrocene indicate that there are two types of solvation around the molecule,<sup>28</sup> solvation directed toward the center of cyclopentadienyl ring and direct solvation involving the iron center of ferrocene (parts a and c of Figure 1). Two interactions where the solvent acts as an acid and Fc as a base are shown in parts a and b of Figure 1; such interactions would be weaker for the  $\text{Fc}^+$  ion.<sup>14</sup> A hydrogen from a solvent molecule may interact with a nonbonding filled orbital of the  $\text{Fe(II)}$  metal center (Figure 1a). The limiting case of this interaction is when a Brønsted acid transfers a proton to the iron center in an oxidative addition reaction to form the  $\text{Fe(IV)}$  hydride,  $[\text{Fe}(\text{Cp})_2\text{H}]^+$ .<sup>29,30</sup> Another possible interaction is hydrogen bonding between the hydrogens of the solvent with the  $\text{Cp}^-$  rings (Figure 1b). Alternatively, the solvent may also act as a base toward the  $\text{Fc}^+$  ion (parts c and d of Figure 1) and to a lesser extent Fc. A solvent molecule may form a weak bond at the equatorial position of the 17-electron  $\text{Fe(III)}$  center of the  $\text{Fc}^+$  ion (Figure 1c),<sup>14,31</sup> or it may also form hydrogen bonds



**Figure 2.** A  $\pi$ -stacking interaction between an aromatic solvent and ferrocene.

with the  $\text{Cp}^-$  ring protons (Figure 1d). In aromatic solvents,  $\pi$ -stacking interactions between the aromatic group of the solvent and the  $\text{Cp}^-$  groups of the complex may also occur (Figure 2).

The  $\text{Me}_{10}\text{Fc}^{+/0}$  couple has been proposed previously as an internal redox standard on the basis of its stability to molecular oxygen and other factors.<sup>32</sup> The bulky methyl groups of  $\text{Me}_{10}\text{Fc}^{+/0}$  are expected to cause greater steric interference to both specific and nonspecific interactions between the solute and solvent molecules. X-ray diffraction studies on  $\text{Fc}$ <sup>33</sup> and  $\text{Me}_{10}\text{Fc}$ <sup>34</sup> indicate that the inter-ring methyl group contacts of the latter are within van der Waals distances and, hence, the methyl groups would hinder access of the solvent to the metal center and to the  $\text{C}_5$  ring. The electrochemistry of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple has been studied by a number of groups under a variety of conditions.<sup>32,35–47</sup> This couple exhibits a reversible one-electron redox process at the electrode with facile electron-transfer kinetics.<sup>38</sup> All of these facts point to the likelihood that the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple will fulfill the requirements proposed by IUPAC for a reference redox system.<sup>8,9</sup> In addition, recent studies on the aqueous electrochemistry of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple showed that, under certain conditions, this couple exhibited reversible responses required to use this as a redox standard in water, as well as nonaqueous solvents.<sup>47</sup> In this paper, the effects of the solvent on the differences in the formal redox potentials of the  $\text{Me}_{10}\text{Fc}^{+/0}$ ,  $\text{Me}_5\text{Fc}^{+/0}$ , and  $\text{Fc}^{+/0}$  couples are evaluated. Additionally, the solvent dependences of the reaction entropies of electron transfer ( $\Delta S_{\text{rc}}$ ) are addressed. The merits of each couple as a redox standard for studying solvent effects on the thermodynamics of electron transfer are also evaluated.

## Experimental Section

**Chemicals.** Chlorobenzene (Ajax chemical, AR grade), 1,2-dichlorobenzene (Merck, AR grade), 1,2-dichloroethane (Merck, AR grade), chloroform (Merck, AR grade), formamide (Fluka AG, p.a.), *N*-methylformamide (Fluka AG, p.a.), ethanol (laboratory grade), 1,2-dibromoethane (Merck, AR grade), bromobenzene (Merck, AR grade), benzyl alcohol (Ajax chemical, 97%), propylene carbonate (Fluka, purum), and nitromethane (Fluka, purum) were purified by literature methods.<sup>48</sup> Nitrobenzene (Aldrich, gold label), aniline (Aldrich, gold label), *N*-methylaniline (Aldrich, gold label), and *N,N*-dimethylaniline (EGA-CHEMIE, GC 99%) were used as received. All other solvents were Aldrich HPLC grade and were used as received. All of the solvents were stored under  $\text{N}_2$  and were purged with argon (CIG, high purity) for at least 30 min before use. The organic solvents used for the spectroscopic measurements had a purity of 99% or better. Water was purified by passing distilled water through a Milli-Q Plus reagent grade water purification system and had a specific resistance of 18.2  $\text{M}\Omega$  cm. For

spectroscopic measurements on  $\text{FcBF}_4$ , all solvents were deoxygenated using Ar. Ferrocene (Merck, for synthesis) was used as received. Decamethylferrocene and 1,2,3,4,5-pentamethylferrocene ( $\text{Me}_5\text{Fc}$ ) were prepared using the methods described elsewhere.<sup>49,50</sup> Decamethylferrocenium tetrafluoroborate was prepared by methods analogous to that used for the preparation of ferrocenium picrate.<sup>47,51</sup> Ferrocenium tetrafluoroborate was prepared by the method described previously.<sup>52</sup> Tetra-1-butylammonium perchlorate (Fluka, electrochemical grade) was used as received. Tetra-1-butylammonium tetrafluoroborate was prepared by neutralization of tetrafluoroboric acid (35% v/v, Merck, extra pure grade) with aqueous tetra-1-butylammonium hydroxide (40% v/v, Aldrich)<sup>53</sup> and was recrystallized three times from ethyl acetate (Merck, AR grade) using anhydrous diethyl ether (Ajax chemical, AR grade dried over Na wire).<sup>54</sup> Tetra-1-butylammonium trifluoromethanesulfonate (TBATFMS) was prepared using a modification of the method described elsewhere.<sup>55</sup>  $\text{CF}_3\text{SO}_3\text{H}$  (Aldrich, used as received, 19.2 g in 50 mL) was reacted with tetra-1-butylammonium hydroxide (Aldrich, 40% v/v, 82.8 g). The resulting white precipitate was recrystallized from hot ethyl acetate/excess *n*-hexane, followed by dissolution of the product in boiling methanol (Merck, AR grade, 50 mL). After being filtered, the solution was added dropwise to distilled water (300 mL) followed by stirring of the precipitate in water for 60 min. The product was collected on a glass frit, then washed with distilled water (100 mL) and *n*-pentane (Merck, for synthesis, 150 mL). After being dried at 60 °C in vacuo overnight, the compound was stored over  $\text{P}_2\text{O}_5$ .

**Instrumentation and Procedures.** Conventional electrochemical experiments were performed using a three-electrode system with BAS-100 or BAS-100B/W electrochemical analyzers or a MacLab/2e. Conventional cyclic staircase voltammetry was conducted at room temperature ( $22 \pm 1$  °C). The working electrode was a gold disk electrode (1 mm diameter), a glassy-carbon disk electrode (BAS, 3 mm diameter), or a Pt disk electrode (BAS, 1.5 mm diameter). The electrodes were polished between each run on a suede cloth (Stuers, DP-Nap) using a suspension of alumina (0.04  $\mu\text{m}$ , Stuers, FF-Alumina) and distilled water. Prior to use, the working electrodes were immersed in the appropriate solvent used in the experiment, and then were polished on dry suede cloth. The reference electrode used was a  $\text{Ag}/\text{AgCl}/\text{KCl}(\text{sat.})$  electrode, and a Pt wire was used as the auxiliary electrode. Fast-scanning electrochemical experiments were conducted using the equipment described elsewhere.<sup>56</sup> Formal redox potentials,  $E_f$ , were calculated from the midpoint of the cathodic and anodic peak potentials observed in the cyclic voltammograms. The  $\Delta S_{\text{rc}}$  values were determined using a nonisothermal cell and instrumentation as described previously.<sup>6,57</sup> The temperature range used was typically 40 °C. All correlation and statistical analyses were performed using least-squares analyses of the data. The programs “stepwise” and “regress” in the statistical package MINITAB<sup>58,59</sup> were used to perform the statistical analyses. Only the statistically significant parameters ( $t \geq 2$ ) were retained with the “stepwise” program. The correlation is reported with the adjusted correlation coefficient,  $R_{\text{adj}}^2$ , which is an unbiased estimate of  $R^2$  adjusted for degrees of freedom.<sup>59</sup> UV/vis measurements were conducted using a Cary 5E spectrophotometer at a resolution of 0.5 nm. The  $\lambda_{\text{max}}$  values were obtained from the spectra by a deconvolution method using the WIN-IR curve-fitting program.<sup>60</sup>

## Results

The solvent dependences of the formal redox potentials of the  $\text{Fc}^{+/0}$ ,  $\text{Me}_5\text{Fc}^{+/0}$ , and  $\text{Me}_{10}\text{Fc}^{+/0}$  couples were studied in 29

solvents including water. All redox couples were reversible or quasireversible at a scan rate of 100  $\text{mV s}^{-1}$  in all of these solvents. Peak-to-peak separations,  $\Delta E_p$ , ranged from 58 to 90 mV for  $\text{Fc}^{+/0}$ , 59 to 108 mV for the  $\text{Me}_5\text{Fc}^{+/0}$ , and 59 to 93 mV for the  $\text{Me}_{10}\text{Fc}^{+/0}$  couples (Table 1), except for water, where DPV or rotating disk electrode techniques at low concentrations were required to obtain reversible responses.<sup>47</sup> The larger values of the peak-to-peak separations,  $\Delta E_p$ , in the less polar solvents are attributed to incomplete  $iR$  compensation, since the heterogeneous electron-transfer rate constants ( $k_{\text{het}}$ ) are known to be large.<sup>4,61</sup> The  $E_f$  values of the couples shift to more negative potentials as the number of methyl substituents on the Cp ring increases,<sup>56</sup> i.e., by  $\sim 500$  mV in going from  $\text{Fc}^{+/0}$  to  $\text{Me}_{10}\text{Fc}^{+/0}$  and  $\sim 250$  mV in going from  $\text{Me}_5\text{Fc}^{+/0}$  to  $\text{Me}_{10}\text{Fc}^{+/0}$ . This trend reflects the enhanced electron donor properties of the ligand with an increase in methyl substitution on the C<sub>5</sub> ring.<sup>62</sup> In all of the solvents, the voltammetric peak currents of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple are less than those of the  $\text{Fc}^{+/0}$  couple at comparable concentrations (Figure 3). This effect is attributed to the much smaller diffusion coefficients of the members of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple.<sup>38,61</sup> The values of  $\Delta E_p$  of both couples are comparable in all solvents studied. Fast-scanning cyclic voltammetry (FSCV) experiments up to 640  $\text{V s}^{-1}$  in acetonitrile show that the cyclic voltammograms (CVs) of both complexes have similar  $\Delta E_p$  values at all scan rates studied (Figure 4, Table 2). Thus, the  $\text{Me}_5\text{Fc}^{+/0}$  and  $\text{Me}_{10}\text{Fc}^{+/0}$  couples have similar heterogeneous electron-transfer rate constants ( $k_{\text{het}}$ ) as the  $\text{Fc}^{+/0}$  couple, which is known to have one of the largest  $k_{\text{het}}$  values measured.<sup>4,61</sup> Previous measurements of the heterogeneous electron-transfer rate constant of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple<sup>38</sup> support these results. In addition, the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple exhibits reversible electron transfer in solvents such as *N*-methylaniline and *N,N*-dimethylaniline, in which the oxidation of Fc is beyond the solvent window.

To minimize complications due to uncertain liquid junction potentials, the formal potentials of the  $\text{Fc}^{+/0}$  and  $\text{Me}_5\text{Fc}^{+/0}$  couples were referenced to the  $E_f$  value of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple (Table 1). The value of  $E_f$  for the  $\text{Fc}^{+/0}$  couple vs  $\text{Me}_{10}\text{Fc}^{+/0}$  shifts about 284 mV (28  $\text{kJ mol}^{-1}$ ) over the range of solvents studied (including water). Of this variation, about 148 mV (15  $\text{kJ mol}^{-1}$ ) was due to values obtained from the organic solvents. The nature of the anion ( $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ) of the background electrolyte had little effect on the value of  $E_f$ ; hence, most of the data reported in Table 1 are those recorded using (*n*-Bu)<sub>4</sub>NClO<sub>4</sub> as the background electrolyte. The value of  $E_f$  of the  $\text{Me}_5\text{Fc}^{+/0}$  couple vs  $\text{Me}_{10}\text{Fc}^{+/0}$  is less variable, changing by 161 mV (16  $\text{kJ mol}^{-1}$ ) in the range of solvents studied, but only 89 mV (8.6  $\text{kJ mol}^{-1}$ ) in the organic solvents. These results show that the values of  $E_f$  are quite sensitive to the nature of the solvent. Since the values represent differences in redox potentials, the variations in the absolute values of  $E_f$  of the  $\text{Fc}^{+/0}$  and  $\text{Me}_5\text{Fc}^{+/0}$  couples are probably larger than those indicated above.

There are no clear trends in the  $\Delta S_{\text{rc}}$  values across each series of couples, although  $\Delta S_{\text{rc}}$  values for the  $\text{Me}_5\text{Fc}^{+/0}$  couple tend to be somewhat more positive (Table 3). For a given couple, the value becomes more negative in solvents that have the ability to be hydrogen-bonding acids.

To evaluate the specific and nonspecific solvent interactions that influence the redox potentials of the couples, statistical analyses of the dependences of the  $E_f$  values for the  $\text{Fc}^{+/0}$  and  $\text{Me}_5\text{Fc}^{+/0}$  couples vs  $\text{Me}_{10}\text{Fc}^{+/0}$  on known solvent parameters<sup>15,63</sup> were performed. Since the  $E_f$  values of the  $\text{Me}_5\text{Fc}^{+/0}$  and  $\text{Fc}^{+/0}$  couples in water were very different from those in aqueous

TABLE 1: Reduction Potentials of Me<sub>n</sub>Fc<sup>+/0</sup> Couples in Various Solvents

solvent	Me <sub>10</sub> Fc <sup>+/0a</sup> (mV)	ΔE <sub>p</sub> <sup>b</sup> (mV)	Me <sub>3</sub> Fc <sup>+/0a</sup> (mV)	ΔE <sub>p</sub> <sup>b</sup> (mV)	Fc <sup>+/0a</sup> (mV)	ΔE <sub>p</sub> <sup>b</sup> (mV)	Me <sub>5</sub> Fc <sup>+/0c</sup> (mV)	Fc <sup>+/0c</sup> (mV)
water	-98 ± 5 <sup>d</sup>		26 ± 4 <sup>d</sup>		195 ± 4 <sup>d</sup>		124 ± 4 <sup>d</sup>	291 ± 4 <sup>d</sup>
tetrahydrofuran	202 ± 8 <sup>e</sup>	66	398 ± 2 <sup>e</sup>	71	629 ± 9 <sup>e</sup>	69	196 ± 1 <sup>e</sup>	427 ± 2 <sup>e</sup>
2-propanol	55 ± 4 <sup>f</sup>	59	269 ± 2 <sup>f</sup>	59	511 ± 5 <sup>f</sup>	74	214 ± 2 <sup>f</sup>	455 ± 3 <sup>f</sup>
N,N-dimethylacetamide	127 ± 2 <sup>e</sup>	59	338 ± 3 <sup>e</sup>	59	582 ± 7 <sup>e</sup>	63	211 ± 1 <sup>e</sup>	455 ± 8 <sup>e</sup>
N,N-dimethylformamide	86 ± 1 <sup>e</sup>	59	301 ± 2 <sup>e</sup>	59	544 ± 2 <sup>e</sup>	67	215 ± 5 <sup>e</sup>	458 ± 3 <sup>e</sup>
dimethyl sulfoxide	37 ± 2 <sup>e</sup>	66	255 ± 2 <sup>e</sup>	66	505 ± 2 <sup>e</sup>	65	218 ± 2 <sup>e</sup>	468 ± 1 <sup>e</sup>
ethanol	7 ± 2 <sup>e</sup>	59	226 ± 2 <sup>e</sup>	59	479 ± 2 <sup>e</sup>	69	219 ± 1 <sup>e</sup>	473 ± 2 <sup>e</sup>
1,2-dibromoethane	129 ± 7 <sup>e</sup>	87	364 ± 2 <sup>e</sup>	67	604 ± 5 <sup>e</sup>	80	235 ± 2 <sup>e</sup>	475 ± 7 <sup>e</sup>
acetone	44 ± 4 <sup>e</sup>	59	270 ± 2 <sup>e</sup>	59	525 ± 4 <sup>e</sup>	64	226 ± 2 <sup>e</sup>	479 ± 4 <sup>e</sup>
chloroform	70 ± 1 <sup>e</sup>	64	311 ± 2 <sup>e</sup>	71	553 ± 1 <sup>e</sup>	66	241 ± 2 <sup>e</sup>	483 ± 1 <sup>e</sup>
bromobenzene	114 ± 4 <sup>e</sup>	76			603 ± 3 <sup>e</sup>	90		489 ± 4 <sup>e</sup>
propylene carbonate	-23 ± 3 <sup>e</sup>	59	207 ± 2 <sup>e</sup>	59	472 ± 2 <sup>e</sup>	63	230 ± 3 <sup>e</sup>	495 ± 2 <sup>e</sup>
chlorobenzene	103 ± 2 <sup>e</sup>	68	344 ± 2 <sup>e</sup>	90	600 ± 2 <sup>e</sup>	86	241 ± 3 <sup>e</sup>	497 ± 1 <sup>e</sup>
methanol	-78 ± 2 <sup>e</sup>	59	160 ± 2 <sup>e</sup>	59	418 ± 2 <sup>e</sup>	59	238 ± 3 <sup>e</sup>	497 ± 2 <sup>e</sup>
acetonitrile	1 ± 1 <sup>e</sup>	59	235 ± 2 <sup>e</sup>	59	507 ± 2 <sup>e</sup>	59	236 ± 2 <sup>e</sup>	505 ± 2 <sup>e</sup>
benzyl alcohol	-103 ± 2 <sup>e</sup>	62	140 ± 3 <sup>e</sup>	61	406 ± 1 <sup>e</sup>	68	243 ± 6 <sup>e</sup>	508 ± 3 <sup>e</sup>
N-methylformamide	-54 ± 2 <sup>e</sup>	60			456 ± 1 <sup>e</sup>	61		510 ± 2 <sup>e</sup>
formamide	-175 ± 3 <sup>e</sup>	59	69 ± 5 <sup>e</sup>	59	335 ± 1 <sup>e</sup>	103	244 ± 2 <sup>e</sup>	510 ± 3 <sup>e</sup>
nitrobenzene	-17 ± 5 <sup>e</sup>	59	231 ± 2 <sup>e</sup>	59	497 ± 4 <sup>e</sup>	60	248 ± 1 <sup>e</sup>	514 ± 2 <sup>e</sup>
nitromethane	-111 ± 4 <sup>e</sup>	61	127 ± 3 <sup>e</sup>	64	403 ± 4 <sup>e</sup>	61	238 ± 2 <sup>e</sup>	516 ± 4 <sup>e</sup>
pyridine	68 ± 5 <sup>e</sup>	59	318 ± 2 <sup>e</sup>	59	587 ± 4 <sup>e</sup>	59	250 ± 1 <sup>e</sup>	517 ± 4 <sup>e</sup>
benzonitrile	-28 ± 4 <sup>e</sup>	60	219 ± 5 <sup>e</sup>	59	495 ± 3 <sup>e</sup>	67	247 ± 1 <sup>e</sup>	523 ± 1 <sup>e</sup>
aniline	-157 ± 6 <sup>e</sup>	59	94 ± 2 <sup>e</sup>	60	369 ± 5 <sup>e</sup>	138	251 ± 4 <sup>e</sup>	527 ± 4 <sup>e</sup>
N-methylaniline	-67 ± 3 <sup>e</sup>	89						
N,N-dimethylaniline	127 ± 2 <sup>e</sup>	93	348 ± 2 <sup>e</sup>	106			221 ± 1 <sup>e</sup>	-
dichloromethane	-12 ± 4 <sup>e</sup>	60	261 ± 2 <sup>e</sup>	59	520 ± 3 <sup>e</sup>	60	273 ± 2 <sup>e</sup>	532 ± 2 <sup>e</sup>
1,2-dichloroethane	-7 ± 1 <sup>e</sup>	59	260 ± 2 <sup>e</sup>	59	525 ± 1 <sup>e</sup>	66	267 ± 2 <sup>e</sup>	532 ± 1 <sup>e</sup>
1,2-dichlorobenzene	74 ± 2 <sup>e</sup>	67	336 ± 2 <sup>e</sup>	65	609 ± 2 <sup>e</sup>	82	262 ± 2 <sup>e</sup>	535 ± 1 <sup>e</sup>
2,2,2-trifluoroethanol	-426 ± 2 <sup>e</sup>	72	-141 ± 2 <sup>e</sup>	61	157 ± 2 <sup>e</sup>	61	285 ± 1 <sup>e</sup>	575 ± 4 <sup>e</sup>

<sup>a</sup> Reduction potential ( $E_f$ ) in mV vs Ag/AgCl/KCl (sat.) at 22 ± 1 °C. <sup>b</sup> Scan rate = 100 mV s<sup>-1</sup>,  $iR$  compensated 80–100%. <sup>c</sup> Reduction potential ( $E_f$ ) in mV vs Me<sub>10</sub>Fc<sup>+/0</sup> couple at 22 ± 1 °C. <sup>d</sup> Obtained using differential pulse voltammetry in 0.1 M NaF; the same value is obtained in 0.1 M NaClO<sub>4</sub>. <sup>e</sup> 0.1 M (*n*-Bu)<sub>4</sub>NClO<sub>4</sub>. <sup>f</sup> 0.1 M (*n*-Bu)<sub>4</sub>NCF<sub>3</sub>SO<sub>3</sub>.

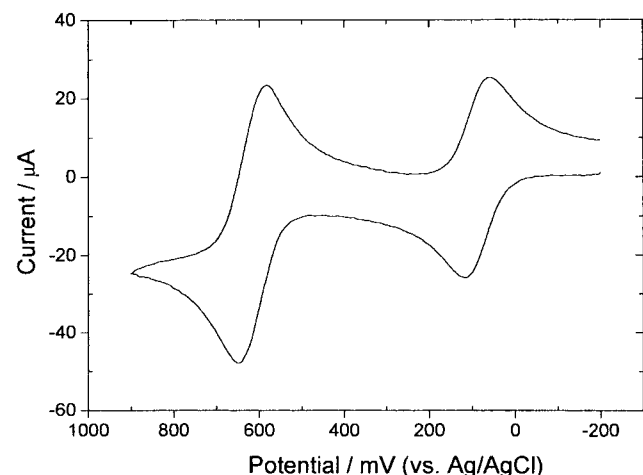


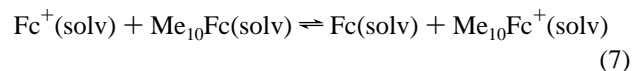
Figure 3. Cyclic voltammograms of Fc<sup>+/0</sup> and Me<sub>10</sub>Fc<sup>+/0</sup> couples (each 2 mM) in a solution of 0.1 M (*n*-Bu)<sub>4</sub>NClO<sub>4</sub> in 1,2-dichloroethane; scan rate 100 mV s<sup>-1</sup>;  $T = 25$  °C.

solvents, the statistical analyses were performed with and without the data in aqueous solution. Due to possible  $\pi$ -stacking interactions between the redox couples and the aromatic solvents, the statistical analyses were also conducted using the data within a class of solvents, viz. aliphatic and aromatic solvents.

The statistical analyses of the solvent dependences of the  $E_f$  values of the Fc<sup>+/0</sup> couple using eq 2, and the Fawcett model,<sup>23</sup> are summarized in Tables S1–S5 and S6–S10 of the Supporting Information, respectively. Statistical analyses using eq 2 and data obtained from all solvents except water gave eq 6 as the most statistically significant correlation ( $R_{\text{adj}}^2 = 61.0\%$ ,  $n =$

26) for the  $E_f$  values defined by eq 7.

$$E_f = 429 + 51.0\alpha - 56.8\beta + 86.6(\pi^* + 0.26\delta) \text{ (mV)} \quad (6)$$



The square of Hildebrand solubility parameter,  $\delta_H^2$ , is the only parameter that does not give a statistically significant contribution to the solvent dependence of  $E_f$  values of the Fc<sup>+/0</sup> couple. The statistical significance of the contributions of the  $\alpha$ ,  $\beta$ ,  $\pi^*$ , and  $\delta$  parameters to the solvent dependence of the  $E_f$  values of the Fc<sup>+/0</sup> couple is given by the  $t$  ratios of 4.44, 3.65, 3.25, and 2.18, respectively.

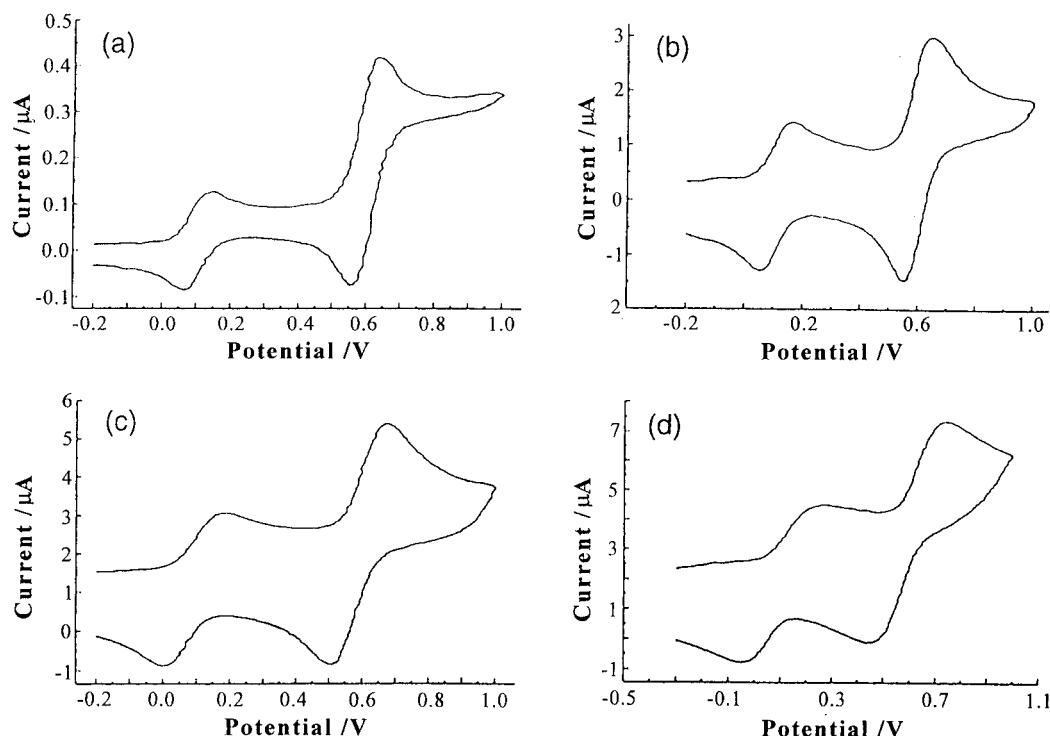
When the aromatic solvents are excluded from the analyses, the most statistically significant correlation (eq 8,  $R_{\text{adj}}^2 = 76.9\%$ ,  $n = 18$ ), between  $E_f$  and the solvent parameters is

$$E_f = 414 + 59.2\alpha - 63.6\beta + 105(\pi^* + 0.24\delta) \text{ (mV)} \quad (8)$$

The contribution of  $\delta$  now becomes insignificant with a  $t$  ratio of 0.85. This is expected since it is a correction for the polarizability of aromatic and chlorinated solvents. The significance of the correlation increases compared to that with all of the solvents. The contributions of the other parameters,  $\alpha$ ,  $\beta$ , and  $\pi^*$ , to the  $E_f$  values of the Fc<sup>+/0</sup> couple are still statistically significant with  $t$  ratios of 5.11, 3.30, and 3.85, respectively.

Statistically significant correlations were obtained when the  $E_f$  value for water was included in the analysis (e.g., eq 9), but the fit was significantly worse,  $R_{\text{adj}}^2 = 42.5\%$  ( $t$  ratios of 2.57, 2.04, 0.62, and 4.08, respectively). A slightly better fit was obtained ( $R_{\text{adj}}^2 = 43.1\%$ ) when the term involving the  $\beta$  parameter was included (eq 10) although this term was not





**Figure 4.** Cyclic voltammograms of the  $\text{Fc}^{+/0}$  and  $\text{Me}_{10}\text{Fc}^{+/0}$  couples (2 mM) in acetonitrile/0.1 M  $(n\text{-Bu})_4\text{NBF}_4$  with scan rates of (a) 3.2, (b) 32, (c) 320, and (d) 640  $\text{V s}^{-1}$ , using a 25  $\mu\text{m}$  diameter Au working electrode and Pt pseudo-reference electrode. No  $iR$  compensation was used.

**TABLE 2:  $\Delta E_p$  Values for the  $\text{Fc}^{+/0}$  and  $\text{Me}_{10}\text{Fc}^{+/0}$  Couples at Various Scan Rates in Acetonitrile/0.1 M  $(n\text{-Bu})_4\text{NBF}_4$  at 25  $^\circ\text{C}$**

scan rate ( $\text{V s}^{-1}$ )	$\text{Fc}^{+/0}$ (mV)	$\text{Me}_5\text{Fc}^{+/0}$ (mV)	$\text{Me}_{10}\text{Fc}^{+/0}$ (mV)
3.2	77		72
32	94		111
102	96	96	96
204	120	121	134
297	134	154	153
320	158		187
640	300		300

**TABLE 3: Reaction Entropies ( $\Delta S_{\text{rc}}$ ) of  $\text{Me}_n\text{Fc}^{+/0}$  Couples in Solution**

solvent	reaction entropy ( $\Delta S_{\text{rc}}$ )/ $\text{J K}^{-1} \text{mol}^{-1}$		
	$\text{Fc}^{+/0}$	$\text{Me}_5\text{Fc}^{+/0}$	$\text{Me}_{10}\text{Fc}^{+/0}$
acetone	$78 \pm 1$	$87 \pm 2$	$70 \pm 3$ (59) <sup>b</sup>
acetonitrile	$47 \pm 2$ (48) <sup>a</sup>	$49 \pm 2$	$29 \pm 2$ (46) <sup>b</sup>
methanol	$-7 \pm 2$ (13) <sup>a</sup>	$4 \pm 1$	$-8 \pm 1$
<i>N,N</i> -dimethylformamide	$54 \pm 1$ (57) <sup>a</sup>	$65 \pm 1$	$52 \pm 1$ (50) <sup>b</sup>
dichloromethane	$15 \pm 1$ (59) <sup>a</sup>	$29 \pm 1$	$13 \pm 1$ (20) <sup>b</sup>
ethanol	$-19 \pm 2$	$-15 \pm 1$	$-31 \pm 1$
<i>N,N</i> -dimethylacetamide	$54 \pm 2$	$67 \pm 2$	$58 \pm 2$
1,2-dichloroethane	$39 \pm 3$	$46 \pm 3$	$59 \pm 2$

<sup>a</sup> 0.1 M tetraethylammonium perchlorate; ref 3. <sup>b</sup> 0.1 M tetrabutylammonium hexafluorophosphate; ref 38a.

significant ( $t$  ratios of 2.53, 1.19, 2.01, 0.19, and 3.97, respectively).

$$E_f = 444 + 67.9\alpha + 124(\pi^* + 0.10\delta) - 126\delta_{\text{H}}^2 \text{ (mV)} \quad (9)$$

$$E_f = 462 + 66.3\alpha - 35.2\beta + 121(\pi^* + 0.03\delta) - 122\delta_{\text{H}}^2 \text{ (mV)} \quad (10)$$

A similar trend exists when statistical analyses were conducted using the data in aliphatic solvents and water (Table S5). The

most significant correlation ( $R_{\text{adj}}^2 = 40.3\%$ ,  $n = 19$ ) obtained was

$$E_f = 402 + 90.0\alpha + 181(\pi^* + 0.21\delta) - 145\delta_{\text{H}}^2 \text{ (mV)} \quad (11)$$

with  $t$  ratios for the parameters of 2.60, 2.19, 0.70, and 3.77, respectively.

The results of the statistical analyses obtained using the Fawcett model<sup>23</sup> are summarized in Tables S6–S10. When all nonaqueous solvents were included in the analyses, the  $R_{\text{adj}}^2$  values were low with the best correlation ( $R_{\text{adj}}^2 = 40.5\%$ ,  $n = 24$ ) being given by eq 12.

$$E_f = 395 + 1.56A_{\text{N}} - 1.39D_{\text{N}} + 340P \text{ (mV)} \quad (12)$$

The contributions of  $A_{\text{N}}$ ,  $D_{\text{N}}$ , and  $P$  to the  $E_f$  values of the  $\text{Fc}^{+/0}$  couple are significant with  $t$  ratios of 3.16, 3.13, and 2.34, respectively. Better correlations were apparent when aromatic solvents were excluded from the analyses. The most statistically significant correlation ( $R_{\text{adj}}^2 = 87.8\%$ ,  $n = 16$ ) between  $E_f$  and the solvent parameters is given by eq 13.

$$E_f = 296 + 1.28A_{\text{N}} - 2.91D_{\text{N}} + 162Y + 295P \text{ (mV)} \quad (13)$$

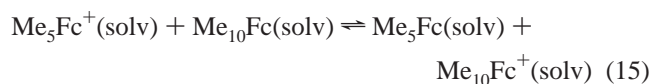
with  $t$  ratios of 4.44, 8.22, 4.71, and 2.04, respectively. No significant correlation was observed when statistical analyses were conducted using the data obtained from aromatic solvents.

Inclusion of the  $E_f$  values in water into the statistical analyses significantly reduced the strength of the correlations (Table S9,  $n = 25$ , and Table S10,  $n = 17$ ). No significant correlation was observed when the analyses were conducted using the data from either aliphatic solvents alone or for all of the solvents studied.

Analysis of the  $\text{Me}_5\text{Fc}^{+/0}$  data using eq 2 showed that the same parameters were statistically significant as those found in the analysis of the  $\text{Fc}^{+/0}$  data, but both the intercept and coefficients are approximately half of those found in eq 6 ( $R_{\text{adj}}^2$

= 68.3%,  $n = 25$ , eq 14). The correlations of the  $E_f$  values of the  $\text{Me}_5\text{Fc}^{+/0}$  couple in organic solvents (defined by eq 15) gave  $t$  ratios of 4.16, 4.93, 2.30, and 2.73, respectively, for the  $\alpha$ ,  $\beta$ ,  $\pi^*$ , and  $\delta$  parameters (Table S11 of the Supporting Information).

$$E_f = 214 + 27.8\alpha - 45.3\beta + 35.6(\pi^* + 0.45\delta) \text{ (mV)} \quad (14)$$



The correlation is improved when only the data in the aliphatic solvents are considered ( $R_{\text{adj}}^2 = 80.1\%$ ,  $n = 17$ ), but the same trends are noticed (eq 16, Table S12 of the Supporting Information). The values of the coefficients were again approximately one-half of those observed for the analogous equation for the  $\text{Fc}^{+/0}$  couple. The  $t$  ratios for the coefficients are 4.83, 2.67, 2.95, and 2.54, respectively.

$$E_f = 191 + 35.6\alpha - 33.6\beta + 51.6(\pi^* + 0.92\delta) \text{ (mV)} \quad (16)$$

No significant correlations were obtained when only the data from aromatic solvents were used (Table S13 of the Supporting Information,  $n = 8$ ). Inclusion of the data in all solvents including water resulted in significant contributions from the  $\delta_{\text{H}}^2$  parameter (Table S14 of the Supporting Information,  $n = 26$ ), which is similar to the results for the  $\text{Fc}^{+/0}$  couple. The most significant correlation ( $R_{\text{adj}}^2 = 58.0\%$ ) obtained when the data from all solvents were used in the statistical analyses was

$$E_f = 233 + 37.4\alpha - 37.2\beta + 56.7(\pi^* + 0.09\delta) - 69.5\delta_{\text{H}}^2 \text{ (mV)} \quad (17)$$

with  $t$  ratios of 2.81, 2.40, 1.86, 0.50, and 4.44 for the  $\alpha$ ,  $\beta$ ,  $\pi^*$ ,  $\delta$ , and  $\delta_{\text{H}}^2$  parameters, respectively. If the data from aromatic solvents were excluded from the analyses, the contribution of the  $\beta$  parameter becomes insignificant (Table S15 of the Supporting Information). The most significant correlation ( $R_{\text{adj}}^2 = 55.7\%$ ,  $n = 18$ ) was now

$$E_f = 184 + 54.5\alpha + 97.2(\pi^* + 0.56\delta) - 83.8\delta_{\text{H}}^2 \text{ (mV)} \quad (18)$$

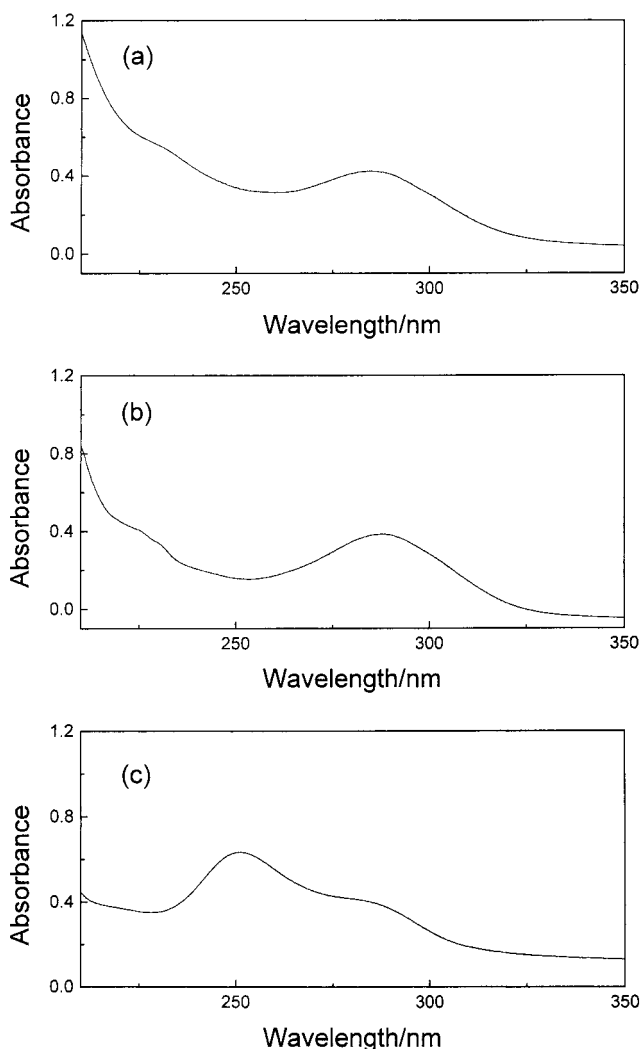
The  $t$  ratios of the  $\alpha$ ,  $\pi^*$ ,  $\delta$ , and  $\delta_{\text{H}}^2$  parameters were 3.06, 2.28, 1.93, and 4.23, respectively.

As was the case for the  $\text{Fc}^{+/0}$  couple, correlations of the  $E_f$  values of the  $\text{Me}_5\text{Fc}^{+/0}$  couple using the Fawcett model resulted in lower values of  $R_{\text{adj}}^2$  with the best correlation given by eq 19 ( $R_{\text{adj}}^2 = 54.6\%$ ;  $t$  ratios, 3.51, 4.01, and 3.11, respectively; Table S16 of the Supporting Information,  $n = 22$ ).<sup>23</sup> For the aliphatic solvents alone, only the contributions of  $A_{\text{N}}$  and  $D_{\text{N}}$  were statistically significant (Table S17 of the Supporting Information,  $n = 15$ ), giving a correlation coefficient of  $R_{\text{adj}}^2 = 75.3\%$  (eq 20;  $t$  ratios, 3.56 and 5.02, respectively).

$$E_f = 166 + 0.954A_{\text{N}} - 1.02D_{\text{N}} + 254P \text{ (mV)} \quad (19)$$

$$E_f = 235 + 0.772A_{\text{N}} - 1.35D_{\text{N}} \text{ (mV)} \quad (20)$$

Solvent effects on both members of each of the  $\text{Fc}^{+/0}$  and  $\text{Me}_{10}\text{Fc}^{+/0}$  redox couples were also studied by electronic absorption spectroscopy. It was anticipated that the differences between the polarity of the ground states and the excited states of the complexes would cause a shift in  $\lambda_{\text{max}}$  of the absorption peaks of the UV/vis spectra of  $\text{Fc}$ ,  $\text{Me}_{10}\text{Fc}$ ,  $\text{FcBF}_4$ , and  $\text{Me}_{10}\text{-FcBF}_4$  with a change of solvent,<sup>22</sup> especially for the charge-



**Figure 5.** Electronic absorption spectra of  $3.7 \times 10^{-5}$  M  $\text{FcBF}_4$  in (a) acetonitrile, (b) methanol, and (c) water.

transfer peaks. The UV/vis spectra of both members of the  $\text{Fc}^{+/0}$  and  $\text{Me}_{10}\text{Fc}^{+/0}$  couples were recorded in a range of solvents: 18 solvents for  $\text{Fc}$ , 18 solvents for  $\text{Me}_{10}\text{Fc}$ , 14 solvents for  $\text{FcBF}_4$ , and 11 solvents for  $\text{Me}_{10}\text{FcBF}_4$ . Negligible shifts (maximum shift was 3 times the experimental error) in the energies of the bands arising from the  $d \rightarrow d$  transitions and the charge-transfer bands were observed in the spectra of  $\text{Fc}$ ,  $\text{Me}_{10}\text{Fc}$ , and  $\text{Me}_{10}\text{FcBF}_4$ .  $\text{FcBF}_4$  was unstable in all solvents studied except water. In organic solvents, the color of the solution changed rapidly when the complex was added to the aerated solvents, indicating decomposition of the complex. Decomposition of ferrocenium ion has been observed previously.<sup>32,64</sup> An interaction with  $\text{O}_2$  was postulated to be important in the decomposition process of the ferrocenium ion.<sup>32,64</sup> In agreement with these reports, no decomposition of  $\text{FcBF}_4$  was apparent when it was dissolved in deoxygenated methanol or acetonitrile. A significant change of the UV/vis spectrum of  $\text{FcBF}_4$  was apparent when the solvent was changed from nonaqueous solvents to water (Figure 5). The shoulder at 225 nm in the nonaqueous solvents shifted bathochromically to 250 nm in water.

Finally, there were statistically significant correlations between the reaction entropies of each of the  $\text{Me}_n\text{Fc}^{+/0}$  couples and either  $\alpha$  or  $A_{\text{N}}$ . The correlation coefficients for these parameters were similar across the series of couples for each

given parameter for the eight solvents studied. The appropriate correlations for the  $\text{Fc}^{+/0}$ ,  $\text{Me}_5\text{Fc}^{+/0}$ , and  $\text{Me}_{10}\text{Fc}^{+/0}$  couples are given by eqs 21 and 22, 23 and 24, and 25 and 26, respectively.

$$\Delta S^\circ = 52.2 - 69.9\alpha \text{ (J K}^{-1} \text{ mol}^{-1}), R_{\text{adj}}^2 = 66.5\%, \\ t = 3.86) \quad (21)$$

$$\Delta S^\circ = 98.1 - 2.81A_N \text{ (J K}^{-1} \text{ mol}^{-1}), R_{\text{adj}}^2 = 89.5\%, \\ t = 7.24) \quad (22)$$

$$\Delta S^\circ = 61.8 - 72.3\alpha \text{ (J K}^{-1} \text{ mol}^{-1}), R_{\text{adj}}^2 = 68.6\%, \\ t = 4.04) \quad (23)$$

$$\Delta S^\circ = 108 - 2.87A_N \text{ (J K}^{-1} \text{ mol}^{-1}), R_{\text{adj}}^2 = 86.9\%, \\ t = 6.38) \quad (24)$$

$$\Delta S^\circ = 52.4 - 79.0\alpha \text{ (J K}^{-1} \text{ mol}^{-1}), R_{\text{adj}}^2 = 73.3\%, \\ t = 4.50) \quad (25)$$

$$\Delta S^\circ = 101 - 3.04A_N \text{ (J K}^{-1} \text{ mol}^{-1}), R_{\text{adj}}^2 = 87.8\%, \\ t = 6.65) \quad (26)$$

## Discussion

**Comparison of Redox Standards.** The suitabilities of the  $\text{Fc}^{+/0}$ ,  $\text{Me}_5\text{Fc}^{+/0}$ , and  $\text{Me}_{10}\text{Fc}^{+/0}$  couples as reference redox systems for the evaluation of solvent effects on the thermodynamics of electron transfer have been assessed. Each of the criteria identified by IUPAC<sup>8,9</sup> as essential in a reference redox system will be addressed in turn. The first recommendation for the reference redox system is that ions or molecules should be spherical with as large a radius as possible. This criterion is met by the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple, since the shape of each member of the couple approximates a sphere and both have much larger radii than those of the  $\text{Fc}^{+/0}$  couple. The second requirement, that the members of the couple should carry low charges, is clearly satisfied by all of the couples discussed here. The third requirement is that the equilibrium at the electrode should be rapid and reversible. Consistent with previous work on the homogeneous and heterogeneous electron-transfer rates of the ferrocenes,<sup>38</sup> the FSCV results (Table 2) show that the value of  $k_{\text{het}}$  for the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple is similar to that of the  $\text{Fc}^{+/0}$  couple. As was reported previously<sup>32,35–46</sup> for the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple, a comparison of  $\Delta E_p$  values for the  $\text{Fc}^{+/0}$ ,  $\text{Me}_5\text{Fc}^{+/0}$ , and  $\text{Me}_{10}\text{Fc}^{+/0}$  couples indicates that the electron-transfer process of this couple at the electrode appears reversible in all solvents studied here. Since the  $\text{Fc}^{+/0}$  couple is electrochemically reversible,<sup>10</sup> the small increases in  $\Delta E_p$  in some solvents are attributed to uncompensated  $iR$  drop. The fourth requirement, which is also met by the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple, is that both members of the redox couple should be soluble in a large range of solvents, including water.<sup>47</sup> The fifth requirement is that minimal geometric change of the ligands should occur as a consequence of the redox state.  $\text{Me}_{10}\text{Fc}^{34}$  and  $\text{Me}_{10}\text{Fc}^{+65}$  have essentially the same molecular structure in the solid state and presumably in solution. The necessity for  $E_f$  to be in an accessible potential range in as many solvents as possible is the sixth requirement for a reference redox system. The enhanced electron-donor capacity of the permethylated cyclopentadienyl ring shifts the formal potential of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple cathodically about 500 mV compared to that of the  $\text{Fc}^{+/0}$  couple. The  $E_f$  value of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple was found to be around 0 mV with respect to the aqueous  $\text{Ag}/\text{AgCl}/\text{KCl}$  (sat.) reference electrode in most solvents. In *N*-methylaniline and *N,N*-dimethylaniline, only the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple exhibits a reversible CV in either solvent. The

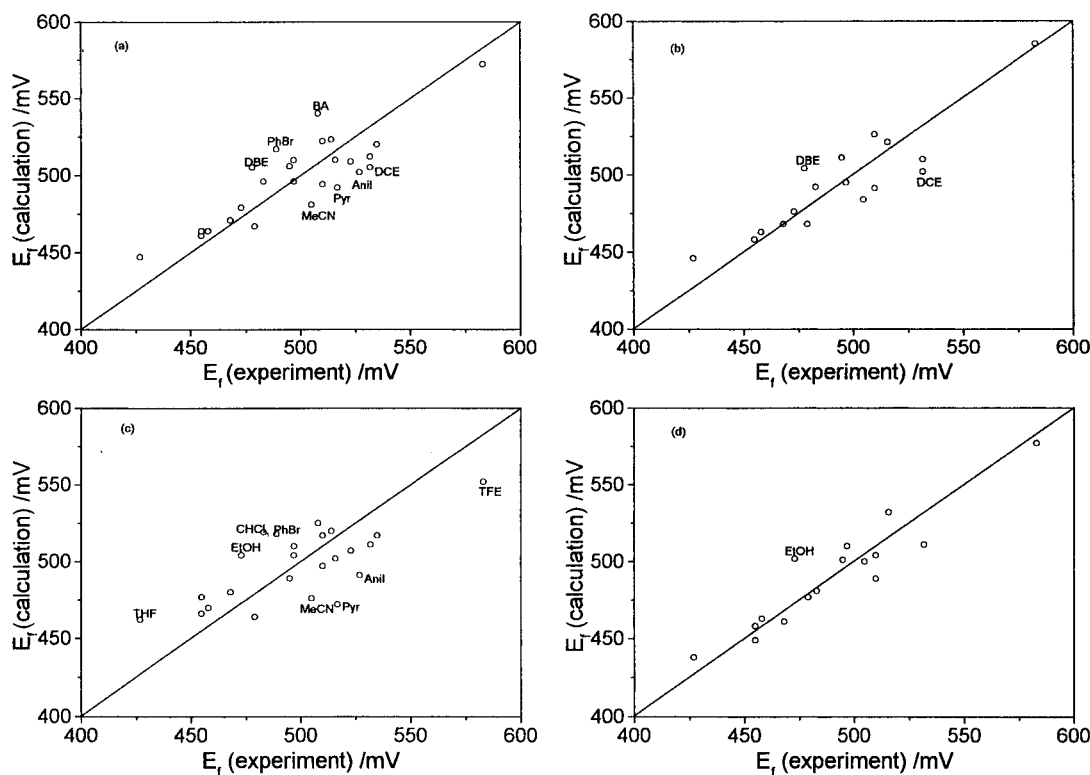
response of the  $\text{Fc}^{+/0}$  couple is not observed within the potential window of these solvents. Furthermore, the value of  $E_f$  for the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple is accessible in practically all solvents, even using the easily oxidized mercury electrode. Both of these facts make this couple superior to the  $\text{Fc}^{+/0}$  couple as a general redox standard, as well as the more specific requirements for ascertaining the solvent dependences of  $E_f$  values of other couples. The last requirement is that both forms should be stable enough to permit potentiometric measurement. Electronic absorption spectroscopic data obtained here show that both components of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple are stable in all of the solvents studied, with or without  $\text{O}_2$  present, at least over a period of 24 h. On the other hand, only the reduced member of the  $\text{Fc}^{+/0}$  couple is stable in all solvents studied over a similar period. Consistent with previous reports,<sup>32,64</sup> the  $\text{Fc}^+$  ion was observed to decompose readily in the presence of aerial  $\text{O}_2$  when the complex was dissolved in all solvents studied, except for water. All of these attributes clearly show that  $\text{Me}_{10}\text{Fc}^{+/0}$  meets all of the requirements proposed for a reference redox system and is superior in most respects to the  $\text{Fc}^{+/0}$  couple as a reference redox standard.

The question as to why a new redox standard should be used if the  $\text{Fc}^{+/0}$  couple is suitable for most solvents lies in the need to understand fundamental solvation effects on the thermodynamics of electron transfer and to find a standard for solvents where the  $\text{Fc}^{+/0}$  couple is inappropriate. To investigate the solvation energies of redox couples and hence single ion solvation energies (in combination with other data), the values of  $E_f$  must be referenced to a couple that has an  $E_f$  value which is ideally independent of the nature of the solvent. The data reported here support the hypothesis that the  $E_f$  values of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple are considerably less solvent dependent than those of the  $\text{Fc}^{+/0}$  couple. These results are consistent with the calculated  $\Delta\Delta G_{\text{solv}}$  values obtained from previous reports.<sup>47,66</sup> The value of  $\Delta\Delta G_{\text{solv}}$  for the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple is much lower than that for the  $\text{Fc}^{+/0}$  couple, indicating that the redox potential of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple is the less sensitive of the two to the nature of the solvent.

In nonaqueous solvents, the  $E_f$  values of the  $\text{Me}_5\text{Fc}^{+/0}$  couple vs the  $\text{Me}_{10}\text{Fc}^{+/0+}$  couple are shifted by about 89 mV over the range of solvents; however, the  $E_f$  values of the  $\text{Fc}^{+/0}$  couple vs the  $\text{Me}_{10}\text{Fc}^{+/0+}$  couple are shifted by about 148 mV using the same solvents. These results suggest strongly that methyl substitution at the  $\text{Cp}^-$  ring is effective in reducing solvent interactions with the members of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple.

**Nature of Solvent Interactions with the  $\text{Me}_n\text{Fc}^{+/0}$  Redox Couples.** Statistical analyses of the contributions of solvent parameters to the redox potential of the  $\text{Fc}^{+/0}$  couple using eq 2 gave better correlations than those of the Fawcett model when all nonaqueous solvents are considered (Figure 6). Nevertheless, using the data from aliphatic solvents, both models show that the value of  $E_f$  for the  $\text{Fc}^{+/0}$  couple is influenced by the hydrogen-bonding acidity, hydrogen-bonding basicity, polarity, and polarizability of the solvents, as predicted by the model. The redox couple involving complexes containing one  $\text{Me}_5\text{Cp}$  ring ( $\text{Me}_5\text{Fc}^{+/0}$  couple) had a substantial reduction in the contributions of these solvent parameters to the solvent dependence of the  $E_f$  values (eq 14). This is consistent with a further reduction in overall solvent interactions with the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple.

The calculated potentials for the  $\text{Fc}^{+/0}$  and  $\text{Me}_5\text{Fc}^{+/0}$  couples in water versus the  $\text{Me}_{10}\text{Fc}^{+/0}$  redox standard (using eqs 6 and 14) are 559 and 260 mV, which are 245 and 140 mV, respectively, greater than the observed values. These deviations indicate that, compared to aliphatic organic solvents, a different



**Figure 6.** Correlations between experimental reduction potentials of the  $\text{Fc}^{+/0}$  couple and those calculated using (a) eq 6, (b) eq 8, (c) eq 12, and (d) eq 13.

solvent/solute interaction dominates in water. The anomalous behavior of water may be explained by the high internal order of water compared with the other solvents used in the study. Clearly, the Hildebrand constant makes a statistically significant contribution when water is included in the solvents used in the correlation (eqs 9, 10, and 18). Because of the anomalous behavior in water, the following discussion will concentrate on the behavior in nonaqueous solvents.

The  $b$  coefficients obtained from the statistical analyses of the  $E_f$  values of both the  $\text{Fc}^{+/0}$  and  $\text{Me}_5\text{Fc}^{+/0}$  couples are negative using either model. Because the  $E_f$  values of the  $\text{Fc}^{+/0}$  couple were referenced to the corresponding  $E_f$  values of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple, the magnitude and sign of the  $b$  coefficients will highlight the differences in the interactions of the solvents acting as Lewis and/or hydrogen-bonding bases with both couples. The values and signs of the  $b$  coefficients determined from the statistical analyses suggest that the Lewis and/or hydrogen-bonding basicity of the solvent stabilizes the oxidized states of the  $\text{Fc}^{+/0}$  and  $\text{Me}_5\text{Fc}^{+/0}$  couples more than that of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple. In correlations using eq 2, the  $b$  coefficient value was about twice that for the  $\text{Fc}^{+/0}$  couple compared with that for the  $\text{Me}_5\text{Fc}^{+/0}$  couple. This suggests that the steric protection offered by the methyl group on one of the  $\text{C}_5$  rings of  $\text{Me}_5\text{Fc}^{+}$  is approximately additive.

In both models, the sign of the  $a$  coefficient is positive, which indicates that hydrogen-bonding acidity provides greater stabilization of the reduced members of the couples. The effect of this stabilization shifts the formal redox potential of both the  $\text{Fc}^{+/0}$  and  $\text{Me}_5\text{Fc}^{+/0}$  couples to more positive values compared with those of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple. The positive contribution of the hydrogen-bonding acidity of the solvent to the formal redox potential supports the notion that  $\text{Fc}$  is stabilized more than  $\text{Me}_5\text{Fc}$ , which in turn is stabilized more than is  $\text{Me}_{10}\text{Fc}$  by this interaction. This observation is again consistent with the steric arguments outlined previously.

The empirical  $\pi^*$  parameter represents a measure of the nonspecific electrostatic interactions between the solvent dipoles and either member of the redox couples. Since the charge distributions within complexes that comprise the  $\text{Me}_n\text{Fc}^{+/0}$  couples are not isotropic, but consist of negative charge densities at the  $\text{Me}_n\text{Cp}$  rings and positive charge densities at the  $\text{Fe}$  centers, the average orientation of the solvent dipoles about the solute will be opposite in the region of the metal and the  $\text{Cp}$  rings. The change in the charge density at the iron center of the  $\text{Fc}^{+/0}$  couple is calculated to be very small ( $\Delta q = 0.08$ );<sup>7</sup> therefore, the main contribution to nonspecific solvent dipole/solute contributions will occur at the  $\text{Cp}$  rings where the largest change in charge density occurs as a result of the redox process. The interactions with the negatively charged  $\text{Cp}$  rings will be stronger for the reduced members of the couples due to their higher charge density, leading to a positive value of the  $c$  coefficient. The steric effect provided by methyl substituents at the  $\text{Cp}$  ring will reduce this interaction resulting in a lower value of the  $c$  coefficient for the  $\text{Me}_5\text{Fc}^{+/0}$  couple.

The contribution of the polarizability correction term,  $\delta$ , is significant when aromatic solvents are included in the analyses. Exclusion of the aromatic solvents from the analyses reduces the significance of the contribution due to  $\delta$ , and the Fawcett model gives a similar result (Figure 6). The contribution of the polarizability parameter,  $P$ , is significant when aromatic solvents are included in the analysis but is insignificant when the analysis is conducted using only aliphatic solvents. These results indicate that there are  $\pi$ -stacking interactions between the ring system of the aromatic solvents and  $\text{Cp}$  rings of the complexes. This interaction is expected to be enhanced in the reduced complexes due to the higher electron density of the  $\text{Cp}$  rings of this state. Methylation of both  $\text{Cp}$  rings reduces this interaction due to steric effects. Stabilization of the reduced member of the  $\text{Fc}^{+/0}$  couple by this interaction will shift the redox potential of this couple anodically relative to that of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple. This



is represented by the positive value of the coefficient of  $\delta$  in eq 6 and of the polarizability parameter in the Fawcett model.

The spectroscopic results reported here give additional support to the hypothesis that the formal redox potential of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple is less solvent dependent than is that of the  $\text{Fc}^{+/0}$  couple. The electronic transitions giving rise to the charge-transfer bands of both members of the  $\text{Me}_{10}\text{Fc}^{+/0}$  and  $\text{Fc}^{+/0}$  couples involve significant changes in the electronic charge distributions within the complexes. The electronic absorption spectra show that only the  $\text{Fc}^+$  ion gives a significant bathochromic shift when the solvent is changed from nonaqueous solvents to water, indicating a stronger solvent/solute interaction between water and  $\text{Fc}^+$ . This result is consistent with a study of the electrochemical behavior of the  $\text{Fc}^{+/0}$  and  $\text{Me}_{10}\text{Fc}^{+/0}$  couples in water.<sup>47</sup> A large cathodic shift in the formal redox potential of the  $\text{Fc}^{+/0}$  couple was observed, indicating a strong stabilization of the oxidized state of the couple. Conversely, the shift in the  $\lambda_{\text{max}}$  values in the electronic absorption spectra of both members of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple is small (experimental error is 0.5 nm), showing that the methyl groups of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple reduce the interactions between water and the complexes of the couple.

The entropy data are also consistent with the proposed solvent effects deduced from the solvent dependences of the  $E_f$  values. Strong hydrogen-bonding acids, such as water and the alcohols, result in low or negative entropies of solvation. This can be contrasted with the value of  $17 \text{ J K}^{-1} \text{ mol}^{-1}$  deduced for the  $\text{Fc}^{+/0}$  couple in the gas phase<sup>67</sup> and is consistent with the strong solvation of  $\text{Fc}$  by such solvents, leading to a reduction in the entropy value compared to the gas phase. By contrast, solvents that have little or no hydrogen-bonding acidity, but are polar hydrogen-bonding bases, have more positive entropy values than the gas-phase value due to electrostriction of the solvent by the cation. The fact that variations in entropy values across the series of couples for a given solvent do not show consistent trends probably arises from competing reductions of solvent organization to both the reduced (hydrogen-bonding acidity) and oxidized (hydrogen-bonding basicity and dipolarity) members of the couples as the degree of methylation is increased.

## Conclusions

The need for an internal redox standard to be soluble in a large range of solvents, but to have its formal redox potential being solvent independent, appears to be contradictory. However, complexes can meet both criteria if the solvent interactions are strong enough to bring about solubility but vary only slightly with oxidation state in order to minimize the dependence of the value of  $E_f$  on the solvent. That  $\text{Me}_{10}\text{Fc}^{+/0}$  has a relatively large size and little scope for specific interactions satisfies the criteria required for it to be a more suitable redox standard than  $\text{Fc}^{+/0}$ . The  $\text{Me}_{10}\text{Fc}^{+/0}$  couple complies with all of the IUPAC requirements for a reference redox standard and is superior in many respects to the IUPAC recommended  $\text{Fc}^{+/0}$  redox system for studying solvent effects on the thermodynamics of electron transfer of other couples. The superiority of the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple as a redox standard compared to the  $\text{Fc}^{+/0}$  couple in the evaluation of the effects of solvation on the  $\text{C}_{60}^{n-/(n+1)-}$  couples has been demonstrated,<sup>68</sup> which adds further evidence in support of the use of this couple. However, there is still a need for an ongoing search for a reference couple that is even less solvent dependent than the  $\text{Me}_{10}\text{Fc}^{+/0}$  couple in order to lead to an improved understanding of solvent effects on the thermodynamics of electron transfer.

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**Supporting Information Available:** Tables of statistical analyses of the solvent dependences of the potentials of the redox couples and the reaction entropies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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