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**SOLVENT EFFECTS OF IONIC LIQUIDS: INVESTIGATION OF FERROCENES AS ELECTROCHEMICAL PROBES**

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3 ELECTROCHEMICAL PROBES  
4

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10 keywords: Solvent effect, Ionic Liquids, Ferrocenes, Electrochemistry, Kamlet-Taft relationships  
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14 INTRODUCTION  
15

16 Ionic Liquids (ILs) or, more precisely, room-temperature Ionic Liquids (RTILs) represent a class of  
17 compounds more and more investigated, not only as non flammable and non volatile solvents for  
18 chemical reactions, but also in a number of electrochemical applications,<sup>[1]</sup> such as, to name a few,  
19 electrochemical mechanical actuator devices,<sup>[2]</sup> dyes-sensitized photoelectrochemical cells,<sup>[3]</sup>  
20 electrochemical supercapacitors,<sup>[4]</sup> fuel cells and lithium-ion batteries,<sup>[5]</sup> and treatment of nuclear  
21 waste.<sup>[6]</sup> Modified ILs have been used as potential electrolytes,<sup>[7]</sup> as electrodes,<sup>[8]</sup> and in  
22 amperometric flow injection analysis.<sup>[9]</sup> Other important applications of ILs are analytical ones,<sup>[10]</sup>  
23 with particular attention to electrochemical sensors,<sup>[11]</sup> protein extraction,<sup>[12]</sup> or desulfurisation of  
24 oils.<sup>[13]</sup> Recent reviews evidence the importance of RTILs in catalysis<sup>[14]</sup> and chemical industry.<sup>[15]</sup>  
25 The question “How polar are Ionic Liquids?” was periodically risen and several attempts have been  
26 made to describe polarity by macroscopic properties<sup>[16]</sup> or empirical parameters.<sup>[17]</sup> Determination of  
27 static dielectric constant classified ILs as solvents of moderate polarity,<sup>[18]</sup> however dielectric  
28 constants are not always adequate to correlate solvent polarity effects.<sup>[16a]</sup> Mixed valence compounds  
29 were used as probes to determine the polarity of 1-butyl-3-methylimidazolium based ILs and the  
30 conclusion was that they are not “exceptionally” polar.<sup>[19]</sup> To define the nature of ILs polarity, the  
31 molar conductivity ratio was used and compared with solvatochromic polarity scales.<sup>[16b]</sup> Dielectric  
32 continuum calculations used to predict solvation dynamics in dipolar liquids were shown to work  
33 poorly for predicting the response in ILs.<sup>[20]</sup> An important discussion of ILs solvation ability and  
34 polarity was recently reported.<sup>[21]</sup>  
35 Physical properties of ILs were investigated both experimentally<sup>[22]</sup> and by calculations<sup>[23]</sup> and were  
36 discussed by Reichardt,<sup>[24]</sup> but no clearcut pattern emerged.  
37 Solvent effect of ILs was also qualitatively assayed in a number of reactions,<sup>[25]</sup> from which  
38 similarities and differences with molecular solvents were discussed.  
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2 Electrochemical reactivity in ambient temperature ILs is also increasingly important:<sup>[1,26]</sup> advantages  
3 and disadvantages of electrochemical studies in room-temperature ILs have been discussed. Among  
4 disadvantages, high cost, difficult purification, and high viscosity are very important. From the  
5 advantages point of view, we can mention the negligible vapour pressure, the wide electrochemical  
6 window,<sup>[27]</sup> the high thermal and chemical stability, the solvating ability, and the possibility to work  
7 in the absence of supporting electrolyte.<sup>[28]</sup> Moreover, it is possible to observe in ILs transient ionic  
8 and radical species that are undetectable in molecular solvents.<sup>[29]</sup> Therefore, it is not surprising that  
9 electrochemical properties are among the physical characteristics determined for newly synthesized  
10 ILs.<sup>[21c,30]</sup> Results of electrochemical reactions appear to depend on the investigated system. For  
11 example, electrochemical oxidation of 2,6-di-*t*-butylphenol gave better results in acetonitrile than in  
12 bmim ILs, either pure or in mixture with organic solvents,<sup>[31]</sup> while, when simple inorganic  
13 molecules were used, the electrochemistry in ILs presented similarities and differences with  
14 molecular solvents, depending on the nature of the redox couple.<sup>[32]</sup> In another study, potential utility  
15 of 1-ethyl-3-methylimidazolium dicyanamide (emimDCA) was evaluated with CuCl.<sup>[33]</sup> It is worth  
16 mentioning a report of an IL that was not only an electrolyte, but also a solvent in  
17 poly(vinylferrocene) redox switching processes.<sup>[34]</sup> Ferrocene-modified ionic liquids in acetonitrile  
18 and in ILs showed a reversible electrochemical behaviour, with responses typical of those for  
19 unmodified ferrocene.<sup>[35]</sup> Electrochemical investigation in ILs may be complicated; for example,  
20 from studies of the influence of CO<sub>2</sub> in solution on the voltammetric currents of the electroactive  
21 species, it was concluded that the voltammetric response in RTILs cannot be assumed to be  
22 independent on other solutes.<sup>[36]</sup>

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32 Voltammetric studies in ILs might offer indications about polarities of these media, but an important  
33 problem is the choice of a reliable reference system, for which IUPAC dictated requirements.<sup>[37]</sup> It  
34 has been demonstrated that the redox couples ferrocene/ferricenium (FcH/FcH<sup>+</sup>) and  
35 decamethylferrocene/ decamethylferrocenium (Me<sub>10</sub>Fc/Me<sub>10</sub>Fc<sup>+</sup>) meet IUPAC requirements in  
36 molecular solvents.<sup>[38]</sup>

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39 After the first extensive investigation on the electrochemical behaviour of FcH/FcH<sup>+</sup> couple in 1-  
40 butyl-3-methyl imidazolium salts, that estimated the solvodynamic radii by measuring diffusion  
41 coefficients,<sup>[39]</sup> a number of papers appeared dealing with various aspects of FcH/FcH<sup>+</sup>  
42 electrochemistry in ILs. The ferrocene/ferrocenium couple was tested as reference redox couple for  
43 aprotic ionic liquids and it was found suitable for that.<sup>[40]</sup> The diffusion coefficient of ferrocene was  
44 not significantly affected by the concentration,<sup>[41]</sup> or nitrogen atmosphere; on the other hand in Ar  
45 atmosphere an increase of diffusion coefficients with respect to vacuum was detected.<sup>[42]</sup> The  
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2 reversible formal potentials and diffusion coefficients of ferrocene were found to be independent of  
3 electrode material, concentration, and technique used for the measurement.<sup>[43]</sup>

4  
5 However, redox potentials of FcH/FcH<sup>+</sup> do vary with solvent, as a consequence of specific  
6 interactions. Taking advantage of this property, the redox potentials of the two couples, FcH/FcH<sup>+</sup>  
7 and Me<sub>10</sub>Fc/Me<sub>10</sub>Fc<sup>+</sup>, in different ionic liquids were measured in order to investigate whether or not  
8 they can be used as probe for ILs polarity. Moreover, such a study was also done with the aim to  
9 explore the possibility to use the correlation (if any) to estimate unknown solvent empirical  
10 parameters.  
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## 16 Experimental Section

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18 Commercial grade molecular solvents were generally dehydrated and distilled according to literature  
19 methods,<sup>[44]</sup> dimethylsulfoxide (DMSO) was partly frozen, discarding the liquid part, and  
20 spectroscopic grade anhydrous *N,N*-dimethylformamide (DMF) was used as such.  
21

22 HPLC pure Ionic Liquids were prepared by anion exchange of the corresponding bromide,<sup>[45]</sup> the  
23 latter being highly pure after repeated crystallizations. The resulting ILs (Scheme 1) were  
24 characterized by <sup>1</sup>H and <sup>13</sup>C NMR, and their identity was confirmed by comparison with literature  
25 data.<sup>[46]</sup> All the ILs have been kept under inert atmosphere and dried before use under vacuum (0.1  
26 mmHg, 60°C) for at least 1 hr.  
27  
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29 Ferrocene was purified by sublimation, commercial decamethylferrocene and ferrocenium  
30 hexafluorophosphate were used as received.  
31

32 <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded with a Bruker Avance AMX 300 instrument, using D<sub>2</sub>O and  
33 CDCl<sub>3</sub> as solvents.  
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### 36 *Voltammetry Experiments*

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38 Electrochemical experiments were carried out using an Amel Instrument 7059 at room temperature. A  
39 Pt disc (2 mm diameter) and a Pt wire were used as working and counter electrode, respectively, and  
40 were polished by standard procedures before use. Saturated calomel electrode (SCE) was used as the  
41 reference. Measurements were reproducible even after months with the same reference electrode, the  
42 highest difference from the average values being ± 5 mV.  
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45 For experiments in molecular solvent, tetrabutylammonium hexafluorophosphate (TBAH) or  
46 tetrabutylammonium bromide (TBAB) were used as supporting electrolytes, depending on the  
47 solubility. When both salts were soluble, the same results were obtained with either.  
48

49 In all the runs ferrocene and decamethylferrocene concentration was the same (1 mM), in order to  
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1 overcome possible concentration effect, as found recently for ferrocene in bmimTf<sub>2</sub>N.<sup>[47]</sup> Ferrocene  
2 and decamethylferrocene solutions were kept under stirring long enough before measurements, to  
3 ensure complete solubilization. Due to solubility problems, a ferrocenium salt was used in water.  
4

5 All the solutions were deoxygenated before use, by bubbling nitrogen. Scan rates were 100 and 200  
6 mV/s, with no significant difference in half-wave potential values, nor in distance between anodic  
7 and cathodic peaks. In selected cases, scan rates were varied in the range 50 - 500 mV/s, the same  
8 results were obtained, within experimental error. All runs were at least duplicated and several cycles  
9 were followed each time. Redox potentials,  $E_{1/2}$ , were calculated from the midpoint of the cathodic  
10 and anodic peak potentials observed in the cyclic voltammograms.  
11

12 The results are reported in the Table 1, as average values of runs at 100 mV/s. Parameters and  
13 physical properties used are also reported. Other parameters were also available,<sup>[48]</sup> however, since  
14 values are quite scattered, we tried, as far as possible, to use data sets obtained by the same method.  
15 One example of cyclic voltammetry is shown in Figures 1 (FcH/FcH<sup>+</sup> in molecular and ionic solvent)  
16 and 2 (Me<sub>10</sub>Fc/Me<sub>10</sub>Fc<sup>+</sup> in molecular and ionic solvent).  
17

18 *insert Figure 1 and Figure 2 here*  
19

20 *insert Table 1 here*  
21

## 22 **Results and Discussion**

23 The redox potentials of ferrocene and decamethylferrocene were determined in some molecular  
24 solvents and in a number of Room Temperature Ionic Liquids (Scheme 1), vs. SCE, at room  
25 temperature.  
26

27 *Insert Scheme 1 here*  
28

29 Both compounds satisfy IUPAC standards, as discussed by Lay,<sup>[38]</sup> who investigated solvent effects  
30 of molecular solvents with the same redox systems. However, our results cannot be directly  
31 compared with Lay's data, because the latter were determined against a Ag/Ag<sup>+</sup> reference.  
32

33 When compared with the data available in the literature for  $E_{1/2(\text{FcH})}$  vs. SCE,<sup>[61]</sup> our results are,  
34 nevertheless, in excellent agreement with those in DMF and bmimBF<sub>4</sub>. The same it is not observed in  
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2 bmimPF<sub>6</sub>, an hydrophobic IL, whose water content is generally not strictly controlled and can be  
3 significantly different.

4 Since oxidation of ferrocenes leads to charged species, it could be anticipated that solvents should  
5 affect redox potentials in that the more polar is the solvent, the easier is the oxidation.  
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8 At first, redox potentials were plotted against solvents physical properties. In particular, with  
9 dielectric constants  $\epsilon_r$ , indicative of polarity (Figure 3), a trend – if not a correlation – may be  
10 observed in molecular solvents, but not in ILs: where redox potentials are significantly different also  
11 when dielectric constants are very similar.  
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15 *Insert Figure 3 here*  
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17 To verify whether this behaviour could be ascribed to viscosity, redox potentials of FcH/FcH<sup>+</sup> and  
18 Me<sub>10</sub>Fc/Me<sub>10</sub>Fc<sup>+</sup> were plotted against this parameter, as shown in Figure 4. From inspection of the  
19 graph, it is apparent that viscosity is not a suitable descriptor for the observed differences of redox  
20 potentials.  
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23 No correlation could be found with macroscopic IL properties, as already found in the literature.<sup>[62]</sup>  
24 Therefore, empirical solvent parameters were tested. A plot of redox potentials vs. solvatochromic  
25 parameter  $E_T^N$  (Figure 5) gave scattered points. The same pattern was shown by others empirical  
26 solvent parameters, such as  $\pi^*$ ,  $\alpha$  and  $\beta$  (Supporting Material, Figures S1-S3). Therefore a  
27 multiparameter approach was tested.  
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32 *Insert Figure 4 and Figure 5 here*  
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35 The multi-parameter Kamlet-Taft equation<sup>[63]</sup> have been relatively little used with RTILs, pure or  
36 mixed with other solvents, with results dependent on the reactions investigated. For example, the  
37 reactivity of anionic nucleophiles with methyl *p*-nitrobenzenesulfonate showed no “IL effect”, with a  
38 correlation indicating hydrogen bond donation by the solvent,<sup>[17c,64]</sup> although an “IL effect” was  
39 evidenced by the change in S<sub>N</sub>2 mechanism of the reaction between charged electrophiles and  
40 charged nucleophiles.<sup>[65]</sup> Another S<sub>N</sub>2 examined by the Kamlet-Taft equation was quaternization of  
41 1-methylimidazole with benzyl halides,<sup>[66]</sup> where six solvents, molecular and ionic, were tested. In  
42 the substitution reaction of cationic Pt(II) complex with thioacetate, reaction rate increases with  
43 increasing hydrogen bond donor ability ( $\alpha$ ) and dipolarity/polarizability ( $\pi^*$ ) of ILs, with no special  
44 “ionic liquid effect”.<sup>[67]</sup> To the same conclusion led the investigation of the base-catalyzed keto-enol  
45 equilibrium with 2-nitrocyclohexanone.<sup>[68]</sup> The esterification of methoxyacetic acid with benzyl  
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1 alcohol in ILs was examined using a multiparameter empirical relationship, but the dominant  
2 parameter resulted to be the solvent hydrogen bond basicity.<sup>[69]</sup>  
3  
4 The Diels-Alder cycloaddition was one of the most studied reactions. In solvent mixtures bmimBF<sub>4</sub>-  
5 water or methanol, solvophobicity, hydrogen-bond donating,  $\alpha$ , and accepting,  $\beta$ , abilities of the  
6 mixtures were the more influential factors.<sup>[70]</sup> When such reaction was investigated in ILs using  
7 multiparameter linear solvation energy relationship, the hydrogen-bonding donation ability of the  
8 cation resulted important.<sup>[56]</sup> Later, a theoretical study of solvent effect on the same reaction  
9 evidenced that the strong asynchronicity of the Diels-Alder reaction in ILs is due to the polarization  
10 effect of the cation.<sup>[71]</sup> Interestingly, also the influence of ionic liquids on polymerization rate of  
11 methyl methacrylate was tested with the Kamlet-Taft equation and found to depend mainly on  $\pi^*$ .<sup>[72]</sup>  
12 In its more complete formulation, the multi-parameter Kamlet-Taft equation contains a contribution  
13 of solvent dipolarity/polarizability ( $\pi^*$ ), a term relative to hydrogen-bond donating ( $\alpha$ ) and accepting  
14 ( $\beta$ ) abilities, and a contribution of the Hildebrand solubility parameter,  $\delta^2$ , that describes the  
15 formation of cavities in the solvent to accommodate the solute. However, we preferred, as in the  
16 examples above, not to consider this latter parameter, since it did not practically affected the redox  
17 potentials (Figure S4 in Supporting Material).  
18 The solvent dependent redox potentials of ferrocene and decamethylferrocene were treated applying  
19 the multiparameter linear free energy relationship in the form of eq.1, analogous to that used in the  
20 literature.<sup>[38]</sup>

$$E(V) = E_0 + s\pi^* + a\alpha + b\beta \quad (1)$$

21 In Lay's work, the uncertainty due to liquid junction potentials was taken into consideration by  
22 correlating the solvent parameters with  $\Delta E$  between ferrocene and decamethylferrocene redox  
23 potentials.<sup>[38]</sup> However, we preferred to treat ferrocene and decamethylferrocene data separately,  
24 because specific interactions with different solvents are, reasonably, quite different.  
25 The analysis was made with redox potentials measured in all the examined solvents (molecular and  
26 ionic) and in molecular solvents only, with the same results. Coefficients of eq.1 are reported in  
27 Table 2, together with those obtained by the same equation with literature data, giving the  
28 relationships of equations 2 (for ferrocene) and 3 (for decamethylferrocene):

$$\text{FcH: } E(V) = 0.58 - 0.23\pi^* - 0.18\alpha + 0.15\beta \quad (2)$$

$$\text{Me}_{10}\text{Fc: } E(V) = 0.19 - 0.36\pi^* - 0.24\alpha + 0.20\beta \quad (3)$$

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49 *Insert Table 2 here*



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2 The correlation improved very slightly, if the  $\delta^2$  parameter was introduced, indicating that the  
3 improvement is only caused by the higher number of parameters. Therefore we preferred to keep  
4 their number as low as possible, to ensure statistical meaning.

5  
6 If we compare the solvent effect of all the solvents with that of molecular solvents (columns 2 and 3),  
7 the same coefficients resulted, within experimental error, especially for ferrocene redox potentials.  
8 This seems to indicate that there is no special "ionic liquid effect". If we compare our data obtained  
9 in molecular solvents with those from literature data in the same solvents (columns 3 and 4), they are  
10 in good agreement, taking into account the different reference electrodes used for the two  
11 measurements sets. This internal coherence makes one comfortable with respect to the consistency of  
12 results as well as to the choice of the reference electrode, SCE vs Pt or Au; in fact, with these latter  
13 electrodes metal reduction and electrode surface modification have been reported.<sup>[1b, 26a,73,74]</sup> Thus, it  
14 is possible to discuss contribution by individual parameters within the Kamlet-Taft relationship.

15  
16 The negative values for the  $\pi^*$  coefficient is easy to explain: the more polar the solvent, the easiest  
17 the oxidation, with ferrocenium species favoured by solvation. It is more difficult to understand the  
18 role of the hydrogen bond accepting ( $\beta$ ) and donating ( $\alpha$ ) ability of the solvents. In fact, at a first  
19 sight,  $\beta$  should be more effective with the oxidized species, favouring oxidation, whilst  $\alpha$  should  
20 work better with the neutral substrates, rendering oxidation more difficult. Coefficients obtained by  
21 the multiparameter approach say just the opposite.

22  
23 Let us consider the  $\alpha$  contribution first. Hydrogen-bond donation from the solvent to ferrocene might  
24 occur toward the non-bonding electron pair on Fe  $d$  orbital or toward the ring  $\pi$  system (Figure 6).

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35 *insert figure 6 here*

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38 Hydrogen-bond with iron atom can be ruled out: in fact, this interaction, that is not possible with  
39 ferrocenium cation, is not consistent with the negative value of coefficient  $a$ . Moreover,  $a$  of  
40 ferrocene is very similar to that of decamethylferrocene (Table 2), whereas the interaction with iron  
41 should be sterically hindered with the latter. Thus, solvent-to-cyclopentadienyl ring hydrogen-bond  
42 bond donation is more likely and the experimental result should be more strictly related to the  
43 peculiar nature of ferrocene and ferrocenium species. A tentative explanation may begin with the  
44 consideration that, upon oxidation, the 18-electrons closed shell of ferrocene becomes the less stable  
45 17-electrons configuration of ferrocenium cation, with consequent increase of the ring-iron distance  
46 (from 1.66<sup>[75]</sup> to 1.70 Å<sup>[76]</sup> in the solid state) and loosening the cyclopentadienyl-iron bond.

1  
2 Therefore, cyclopentadienyl rings might be more electron-rich in the oxidized than in the reduced  
3 form and the  $\alpha$  parameter should ultimately favour oxidation. If this line of reasoning is correct, it  
4 should hold also for  $\beta$  parameter: the more electron-rich the cyclopentadienyl ring is, the less acidic it  
5 is. Consequently, ferrocene should be more efficiently solvated than ferrocenium as far as solvent  
6 hydrogen-bond accepting ability ( $\beta$ ) is concerned, in agreement with the positive value of coefficient  
7  $b$  (Table 2).  
8

9  
10 We realized that the reasoning is counter-intuitive. Therefore, a calculation of HOMO of ferrocene  
11 and ferrocenium ion was performed using Spartan '08 DFT UB3LYP method, with LACVP basis  
12 set.<sup>[77]</sup> The output is shown in figure 7, where it is evident the higher electron density of Cp ring of  
13 the oxidized species with respect to the reduced one, thus supporting the above interpretation.  
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19 *insert figure 7 here*  
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22 All considered, the multiparameter Kamlet-Taft equation gave a fair correlation with redox potentials  
23 of ferrocene (Figure 8), a less satisfactory one with decamethylferrocene.  
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27 *Insert Figure here*  
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30 Qualitatively, the equation for decamethylferrocene is the same as that for ferrocene, but the fit is  
31 worst; however, the relationship improves significantly if water is not considered (Figure 9).  
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35 *Insert Figure 9 here*  
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38  
39 It is important to consider that this LFER has been applied to ionic liquids together with molecular  
40 solvents. The relationship indicates that, as far as oxidation of ferrocenes is concerned, specific  
41 interaction of reduced and oxidized species with ILs follow the same rules as with molecular  
42 solvents. Therefore ferrocene can be considered a suitable probe for solvent polarity in  
43 electrochemical measurements, unifying in a single relationship molecular and ionic solvents.  
44  
45 However, it is dangerous to generalize and, with different reactions, solvent effects should be  
46 verified each time.  
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## Conclusions

Ferrocene and decamethylferrocene redox potentials depend on the solvent, with no difference between molecular and ionic solvents, since the same Kamlet-Taft multiparameter relationship describes well specific solvent-solute interactions with both types. Decamethylferrocene gave a correlation less satisfactory than ferrocene, thus suggesting that each compound may present different problems in interaction with solvents. Ferrocene emerges as the substrate to be used as a probe for solvent properties.

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2 ABSTRACT

3 The redox potentials of ferrocene and decamethylferrocene were determined in a number of  
4 molecular and ionic solvents and used as a probe for polarity of room temperature ionic liquids. No  
5 macroscopic solvent property is simply related to redox potentials. Single empirical solvent  
6 parameters also are not able to describe the differences in potentials. Instead, Kamlet-Taft  
7 multiparameter relationship fits well ferrocenes redox potentials variation, with both molecular  
8 solvents and ionic liquids, well describing specific solvent-solute interactions with the two probes.  
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## SOLVENT EFFECTS OF IONIC LIQUIDS: INVESTIGATION OF FERROCENES AS ELECTROCHEMICAL PROBES

Claudia Bizzarri, Valeria Conte, Barbara Floris, Pierluca Galloni

Table 1. Redox potentials of ferrocene (FcH) and decamethylferrocene (Me<sub>10</sub>Fc) in different solvents and empirical solvent parameters used.

	Solvent	$\eta$ , mPa s	$\epsilon$	$E_T^N$	$\pi^*$	$\alpha$	$\beta$	$\delta^2 J \text{ cm}^{-3}$	$E_{1/2}(\text{FcH}),$ V	$E_{1/2}(\text{Me}_{10}\text{Fc}),$ V
n.										
1	H <sub>2</sub> O	0.890 <sup>[49]</sup>	78.4 <sup>[16a]</sup>	1.000 <sup>[50]</sup>	1.09 <sup>[17a,51]</sup>	1.17 <sup>[17a, 51]</sup>	0.47 <sup>[17a,51]</sup>	2294 <sup>[52]</sup>	0.212	-0.048
2	EtOH	1.074 <sup>[49]</sup>	24.3 <sup>[16a]</sup>	0.654 <sup>[50]</sup>	0.54 <sup>[51]</sup>	0.86 <sup>[17a]</sup>	0.75 <sup>[17a,50]</sup>	676 <sup>[52]</sup>	0.407	-0.084
3	THF	0.456 <sup>[49]</sup>	7.47 <sup>[51]</sup>	0.207 <sup>[51]</sup>	0.58 <sup>[51]</sup>	0.00 <sup>[51]</sup>	0.55 <sup>[51]</sup>	361 <sup>[52]</sup>	0.580	0.140
4	DMF	0.794 <sup>[49]</sup>	37.06 <sup>[53]</sup>	0.404 <sup>[51]</sup>	0.88 <sup>[51]</sup>	0.00 <sup>[51]</sup>	0.69 <sup>[51]</sup>	581 <sup>[52]</sup>	0.476	0.00
5	DMSO	1.987 <sup>[49]</sup>	46.7 <sup>[15a]</sup>	0.444 <sup>[51]</sup>	1.00 <sup>[51]</sup>	0.00 <sup>[51]</sup>	0.76 <sup>[51]</sup>	708 <sup>[52]</sup>	0.459	-0.039
6	MeCN	0.369 <sup>[49]</sup>	36.2 <sup>[16a]</sup>	0.460 <sup>[51]</sup>	0.75 <sup>[51]</sup>	0.19 <sup>[51]</sup>	0.31 <sup>[51]</sup>	581 <sup>[52]</sup>	0.385	-0.125
7	DCM	0.413 <sup>[49]</sup>	9.05 <sup>[50]</sup>	0.309 <sup>[51]</sup>	0.82 <sup>[51]</sup>	0.13 <sup>[51]</sup>	0.1 <sup>[17a]</sup>	408 <sup>[52]</sup>	0.405	-0.115
8	Me <sub>2</sub> CO	0.306 <sup>[49]</sup>	20.56 <sup>[50]</sup>	0.355 <sup>[51]</sup>	0.71 <sup>[51]</sup>	0.08 <sup>[51]</sup>	0.43 <sup>[17a]</sup>	488 <sup>[52]</sup>	0.483	0.046
9	emimTf <sub>2</sub> N	32.0 <sup>[50]</sup>	12.3 <sup>[16a]</sup>	0.676 <sup>[54]</sup>	0.97 <sup>[17a,55]</sup>	0.659 <sup>[55]</sup>	-	585 <sup>[54]</sup>	0.230	-0.31
10	pmim Tf <sub>2</sub> N	6.402 <sup>[57]</sup>	10.6 <sup>[22d]</sup>	0.654 <sup>[54]</sup>	-	-	-	432,6 <sup>[58]</sup>	0.258	-0.261
11	bmim Tf <sub>2</sub> N	63.572 <sup>[57]</sup>	11.6 <sup>[16a]</sup>	0.642 <sup>[50]</sup>	0.984 <sup>[59]</sup>	0.617 <sup>[59]</sup>	0.243 <sup>[59]</sup>	554 <sup>[54]</sup>	0.270	-0.25
12	hmim Tf <sub>2</sub> N	68.0 <sup>[50]</sup>	7.0 <sup>[54]</sup>	0.654 <sup>[54]</sup>	0.958 <sup>[55]</sup>	0.623 <sup>[55]</sup>	-	555,6 <sup>[58]</sup>	0.250	-0.25
13	bdmim Tf <sub>2</sub> N	88.0 <sup>[50]</sup>	11.6 <sup>[16a]</sup>	0.546 <sup>[54]</sup>	1.01 <sup>[59]</sup>	0.381 <sup>[59]</sup>	0.239 <sup>[59]</sup>	625 <sup>[54]</sup>	0.309	-0.214
14	bupy Tf <sub>2</sub> N	56.8 <sup>[50]</sup>	11.5 <sup>[16a]</sup>	0.648 <sup>[54]</sup>	1.01 <sup>[55]</sup>	0.483 <sup>[55]</sup>	-	-	0.280	-0.25
15	bupy BF <sub>4</sub>	103 <sup>[50]</sup>	11.7 <sup>[16a]</sup>	0.639 <sup>[54]</sup>	-	-	-	-	0.370	-0.03
16	bmim BF <sub>4</sub>	92.0 <sup>[50]</sup>	12.2 <sup>[60]</sup>	0.673 <sup>[50]</sup>	1.09 <sup>[17a]</sup>	0.73 <sup>[50]</sup>	0.55 <sup>[17a]</sup>	929 <sup>[54]</sup>	0.370	-0.08
17	bmim PF <sub>6</sub>	173.0 <sup>[50]</sup>	11.8 <sup>[60]</sup>	0.667 <sup>[50]</sup>	1.02 <sup>[55]</sup>	0.77 <sup>[50]</sup>	0.44 <sup>[17a]</sup>	718 <sup>[54]</sup>	0.270	-0.21

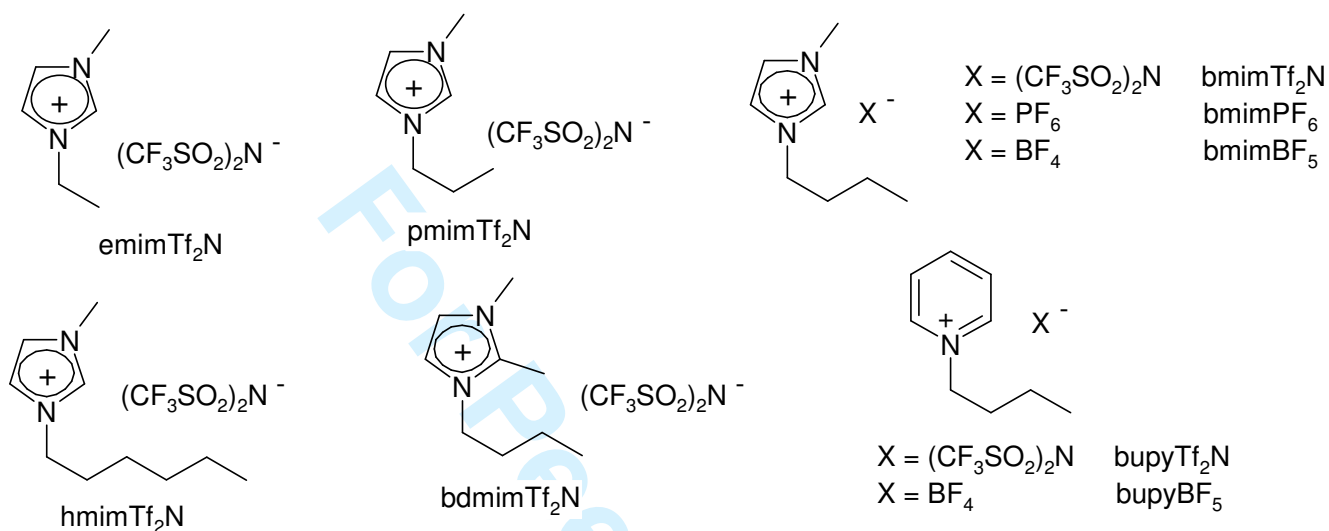
**Table 2.** Coefficients of the multiparameter Kamlet-Taft correlation obtained with ferrocene (FcH) and decamethylferrocene (Me<sub>10</sub>Fc)

parameters	VOCs & ILs	VOCs	Same VOCs, lit. data <sup>[38]a</sup>	All lit. VOCs <sup>[38]a</sup>
<b>FcH</b>				
<i>R</i>	0.980	0.970	0.990	0.949
<i>R</i> <sup>2</sup>	0.959	0.942	0.979	0.900
<i>s</i>	-0.23 ± 0.04	-0.25 ± 0.074	-0.33 ± 0.04	-0.36 ± 0.06
<i>a</i>	-0.18 ± 0.03	-0.18 ± 0.03	-0.21 ± 0.02	-0.25 ± 0.02
<i>b</i>	+0.15 ± 0.03	+0.13 ± 0.06	+0.06 ± 0.04	+0.02 ± 0.02
<i>E</i> <sub>0</sub> (V)	0.583 ± 0.040	0.607 ± 0.060	0.798 ± 0.040	0.843 ± 0.040
<b>Me<sub>10</sub>Fc</b>				
<i>R</i>	0.959	0.959	0.729	0.825
<i>R</i> <sup>2</sup>	0.920	0.920	0.532	0.680
<i>s</i>	-0.36 ± 0.09	-0.56 ± 0.12	-0.32 ± 0.30	-0.38 ± 0.10
<i>a</i>	-0.24 ± 0.04	-0.35 ± 0.06	-0.16 ± 0.10	-0.25 ± 0.05
<i>b</i>	+0.20 ± 0.07	+0.22 ± 0.06	+0.16 ± 0.10	+0.12 ± 0.06
<i>E</i> <sub>0</sub> (V)	0.197 ± 0.090	0.342 ± 0.099	0.158 ± 0.100	0.302 ± 0.099

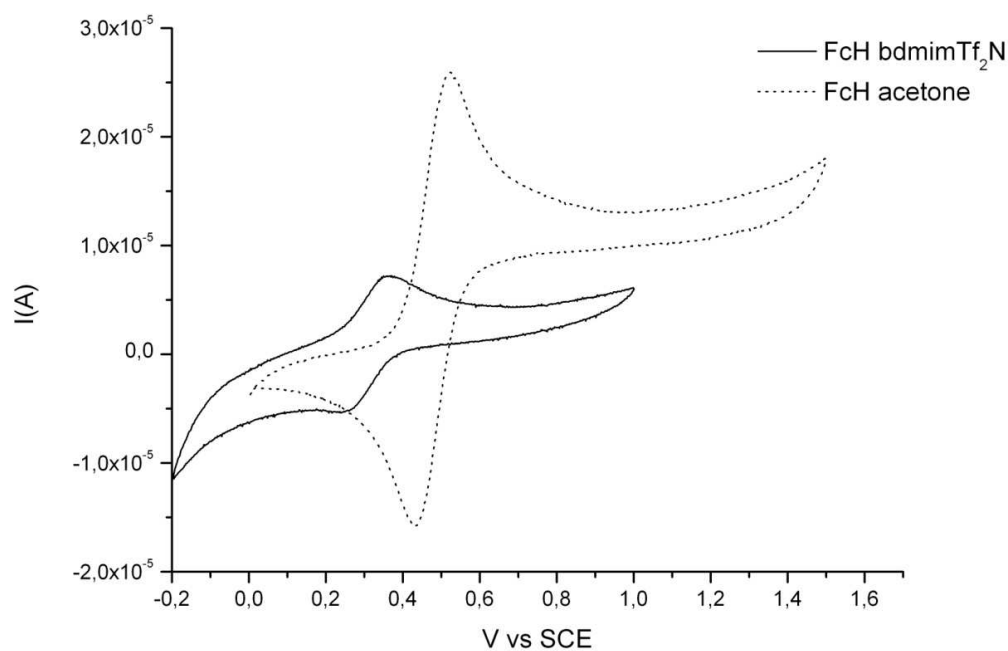
<sup>a</sup> different reference electrode.

SOLVENT EFFECTS OF IONIC LIQUIDS: INVESTIGATION OF FERROCENES AS  
ELECTROCHEMICAL PROBES

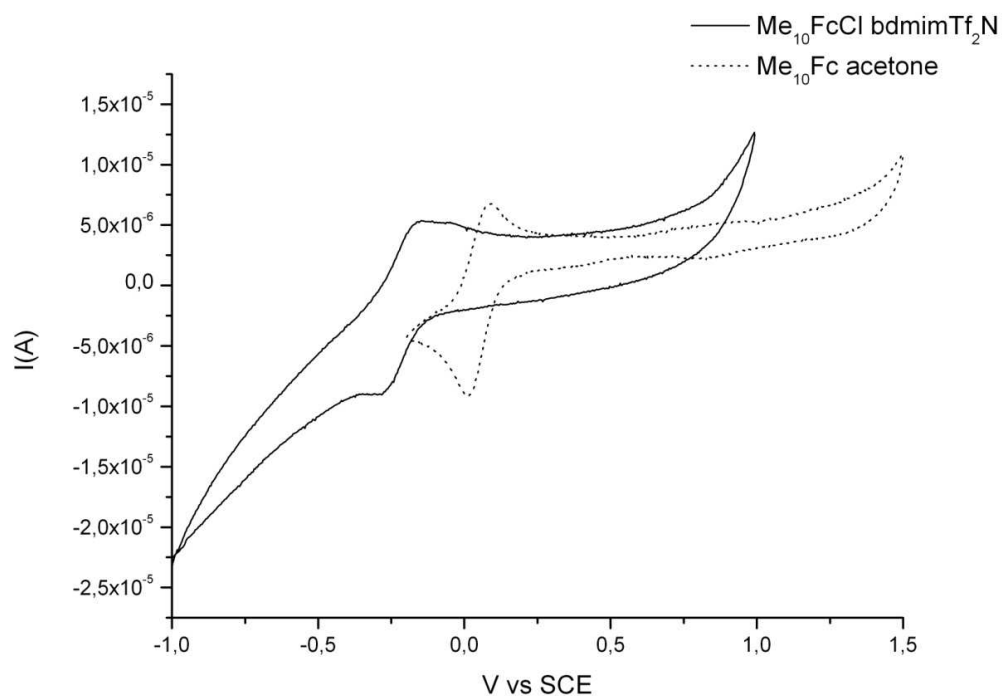
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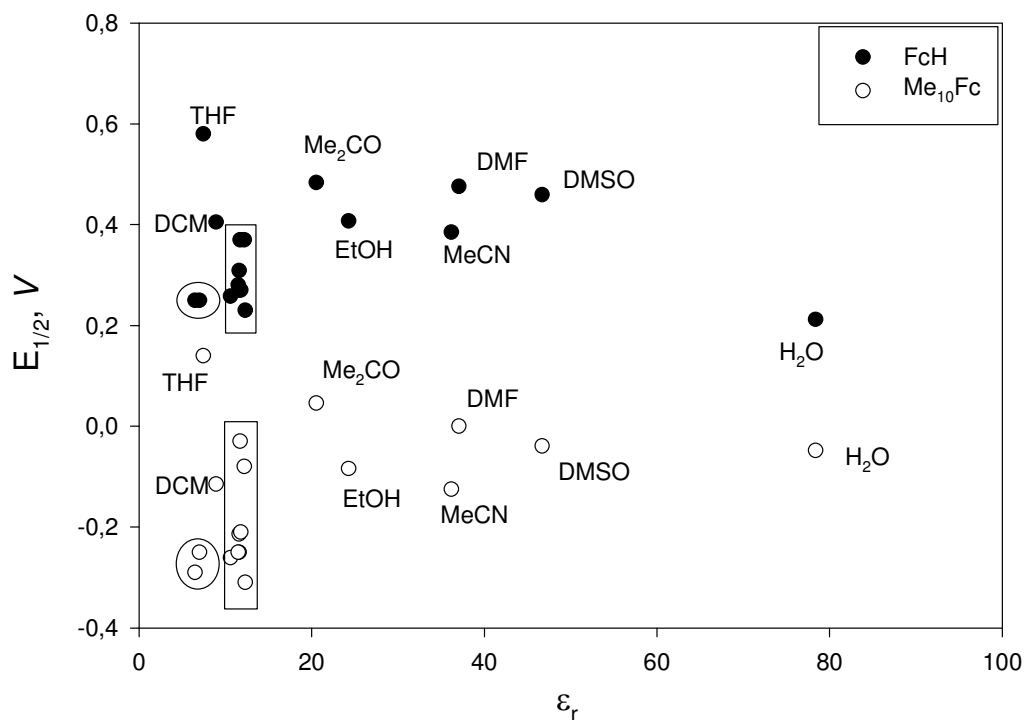
**Scheme 1.** RTILs used as solvents in electrochemical measurements of this paper.



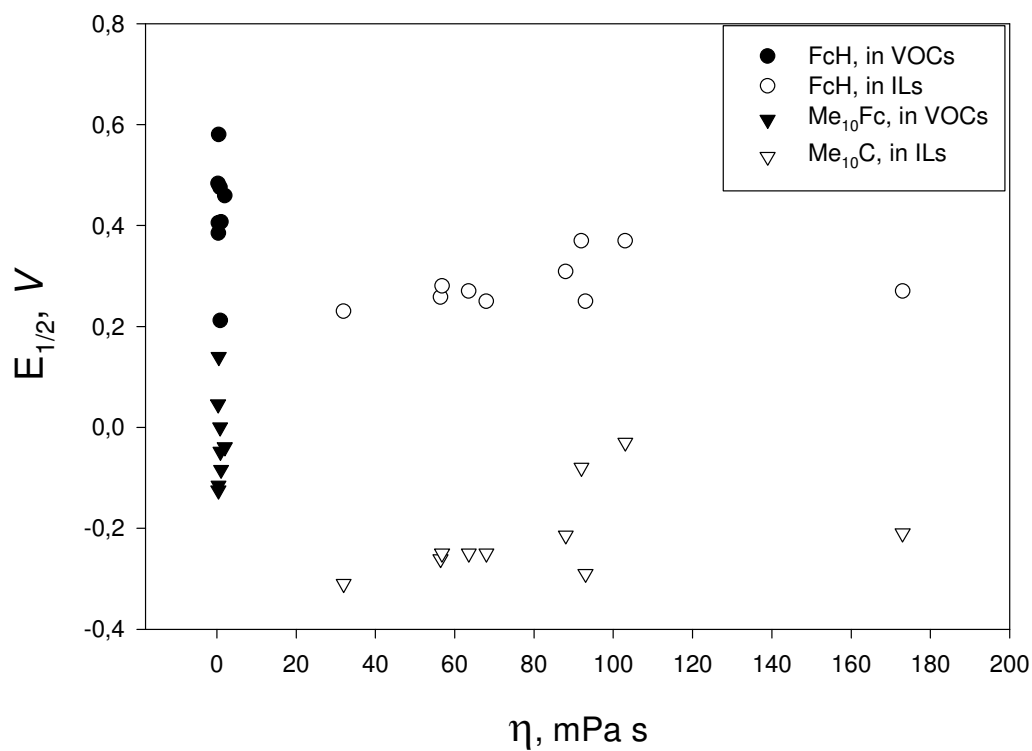
**Figure 1.** CV of  $\text{FcH}/\text{FcH}^+$  in acetone (dotted line) and 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide (solid line); sweep rate, 100 mV/s.



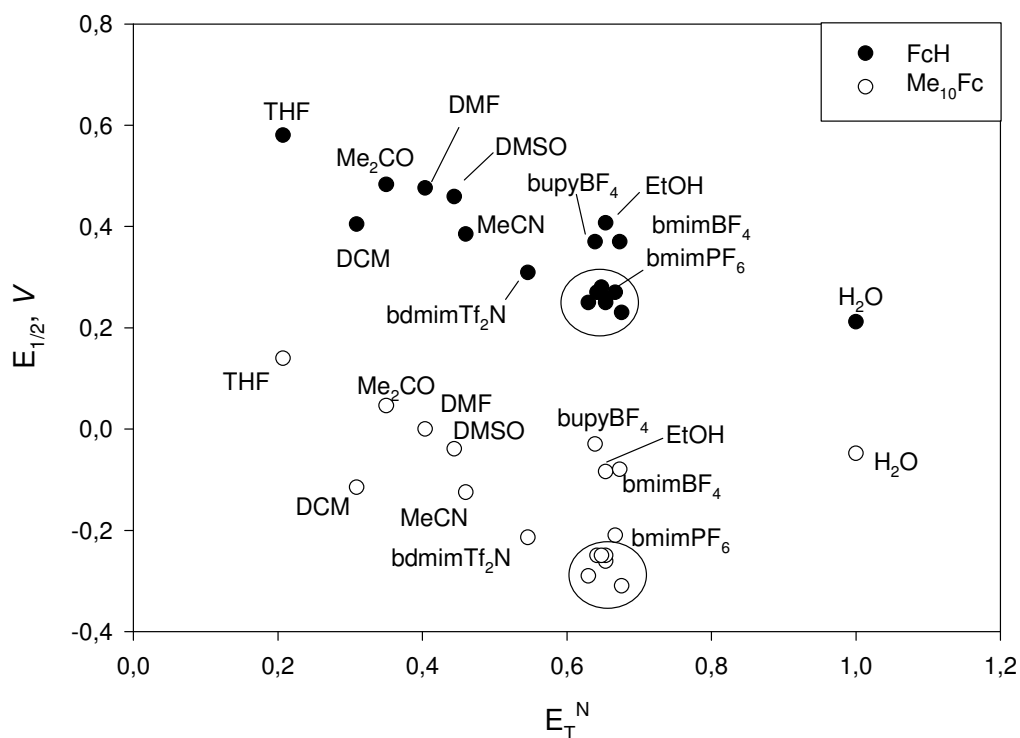
**Figure 2.** CV of  $\text{Me}_{10}\text{Fc}/\text{Me}_{10}\text{Fc}^+$  in acetone (dotted line) and 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide (solid line); sweep rate, 100 mV/s.



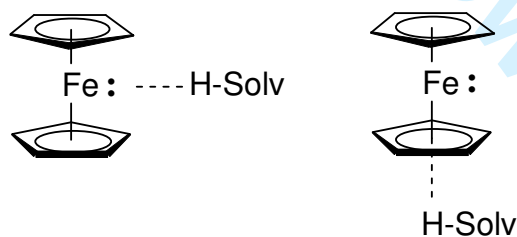
**Figure 3.** Redox potentials of ferrocene (FcH) and decamethylferrocene (Me<sub>10</sub>Fc) vs. static dielectric constant ( $\epsilon_r$ ) values of molecular solvents and ionic liquids; in the circles: hmimTf<sub>2</sub>N and omimTf<sub>2</sub>N; in the rectangles: emimTf<sub>2</sub>N, bmimTf<sub>2</sub>N, bdmimTf<sub>2</sub>N, bupyTf<sub>2</sub>N, bmimBF<sub>4</sub>, bmimPF<sub>6</sub>.



**Figure 4.** Redox potentials of ferrocene (FcH) and decamethylferrocene ( $Me_{10}Fc$ ) vs. viscosity values of molecular and ionic solvents.

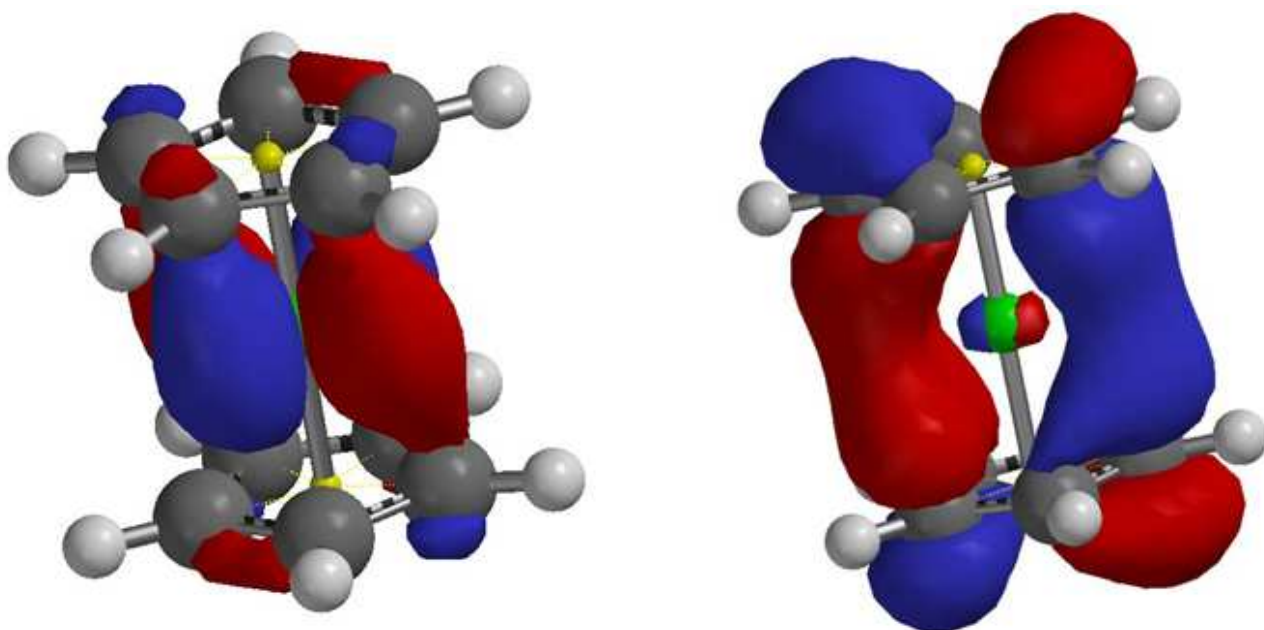


**Figure 5.** Redox potentials of ferrocene (FcH) and decamethylferrocene ( $\text{Me}_{10}\text{Fc}$ ) vs.  $E_T^N$  values of molecular solvents and ionic liquids; in the circles: emimTf<sub>2</sub>N, pmimTf<sub>2</sub>N, bmimTf<sub>2</sub>N, hmimTf<sub>2</sub>N, omimTf<sub>2</sub>N.



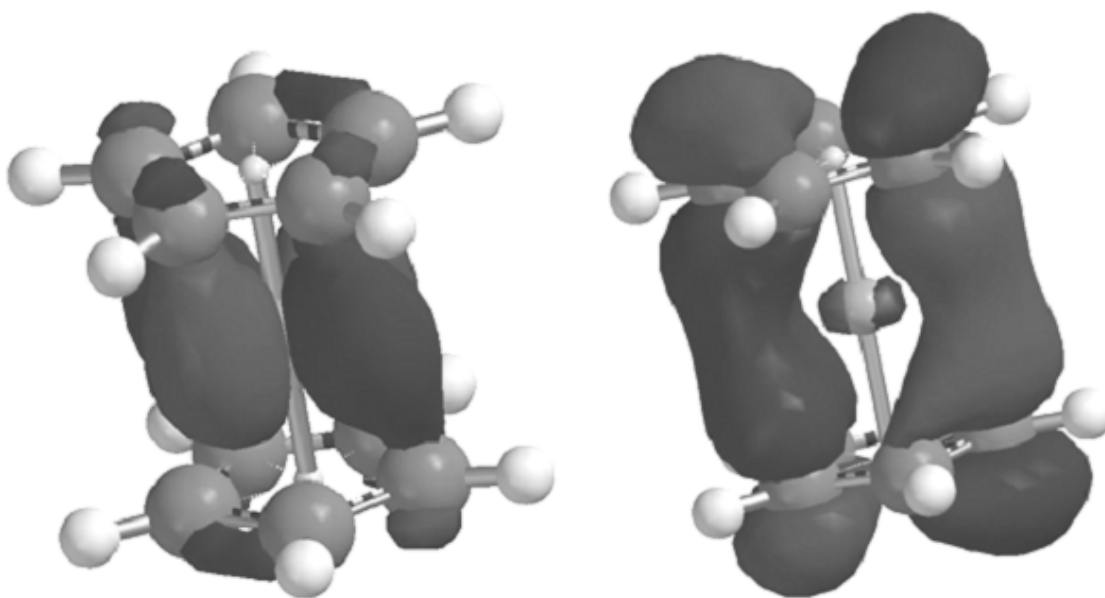
**Figure 6.** Possible hydrogen-bond interactions between ferrocene and donating solvent ( $\alpha$ ).

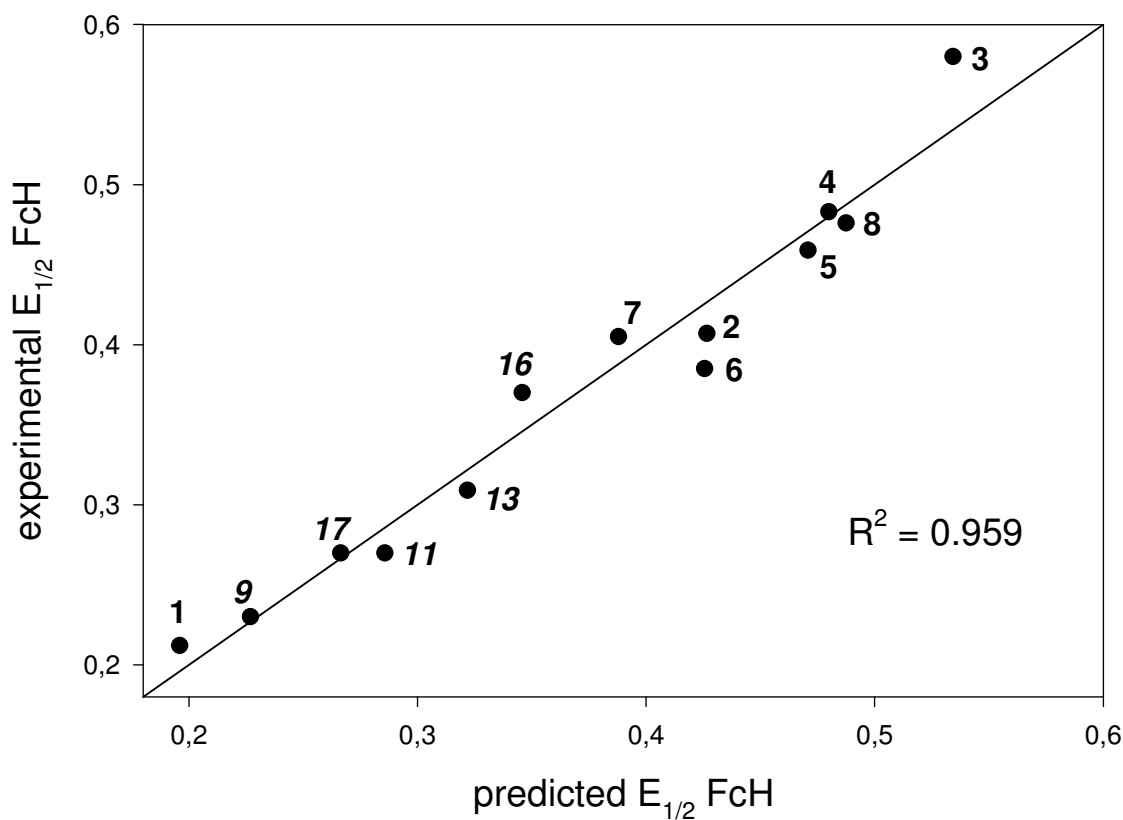




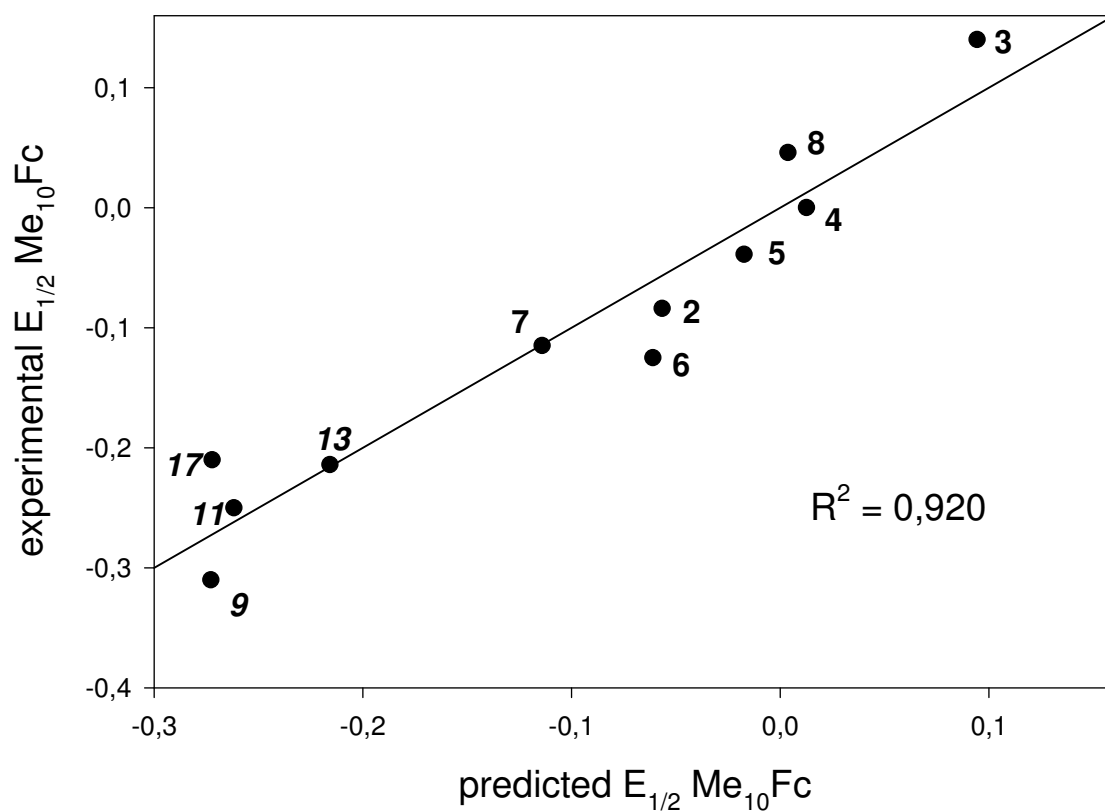
**Figure 7.** DFT calculation of HOMO for ferrocene (left) and ferrocenium ion (right).

Follow B/W version of Figure 7





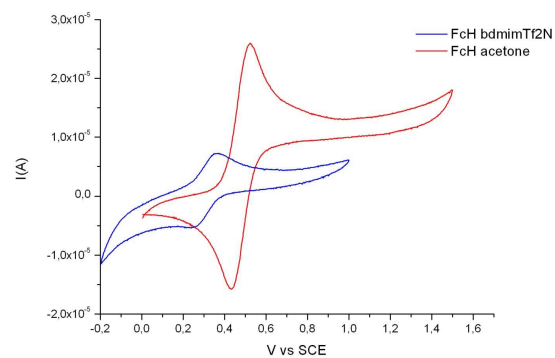
33 **Figure 8.** Experimental redox potentials of ferrocene (Fch) vs. values calculated with the Kamlet-Taft  
34 correlation (numbers refer to solvents, as in Table 1).  
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**Figure 9.** Experimental redox potentials of decamethylferrocene (Me<sub>10</sub>Fc) vs. values calculated with the Kamlet-Taft correlation (numbers refer to solvents, as in Table 1).

## SOLVENT EFFECTS OF IONIC LIQUIDS: INVESTIGATION OF FERROCENES AS ELECTROCHEMICAL PROBES

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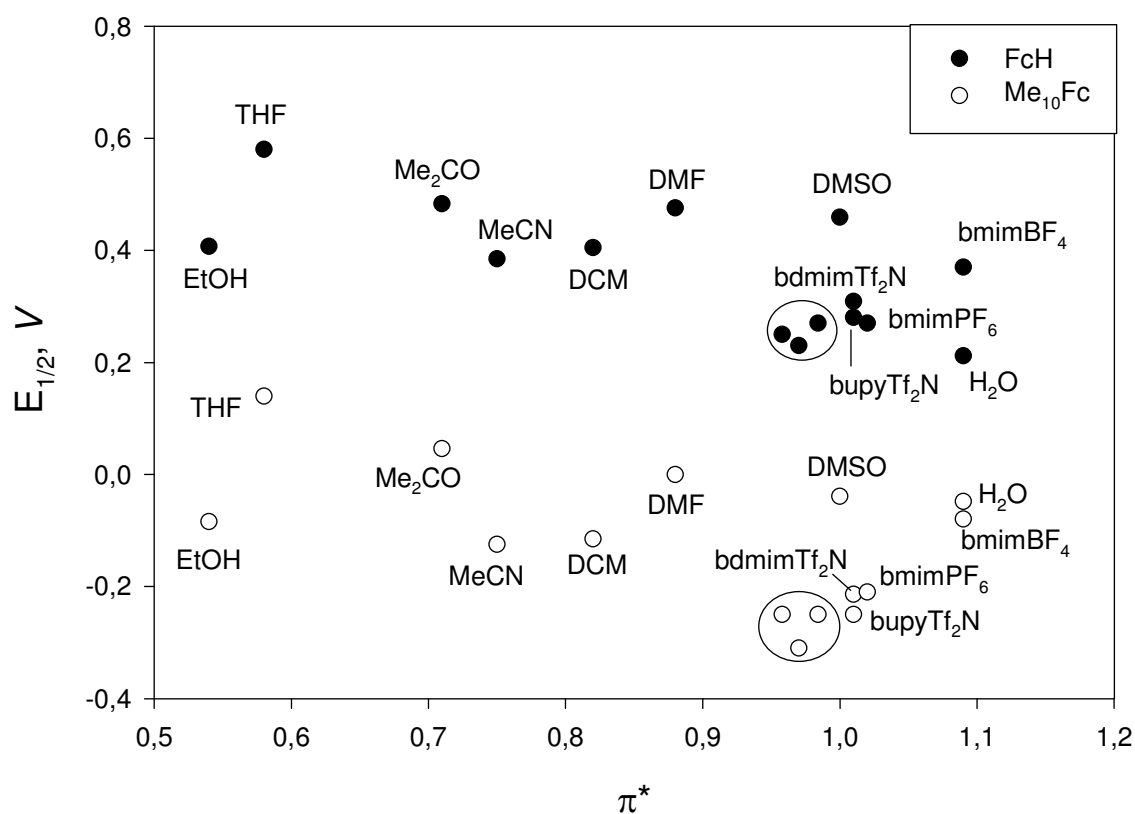


The redox potentials of ferrocene and decamethylferrocene were determined in a number of molecular and ionic solvents and used as a probe for polarity of room temperature ionic liquids. No macroscopic solvent property is simply related to redox potentials. Single empirical solvent parameters also are not able to describe the differences in potentials. Instead, Kamlet-Taft multiparameter relationship fits well ferrocenes redox potentials variation, with both molecular solvents and ionic liquids, well describing specific solvent-solute interactions with both molecules

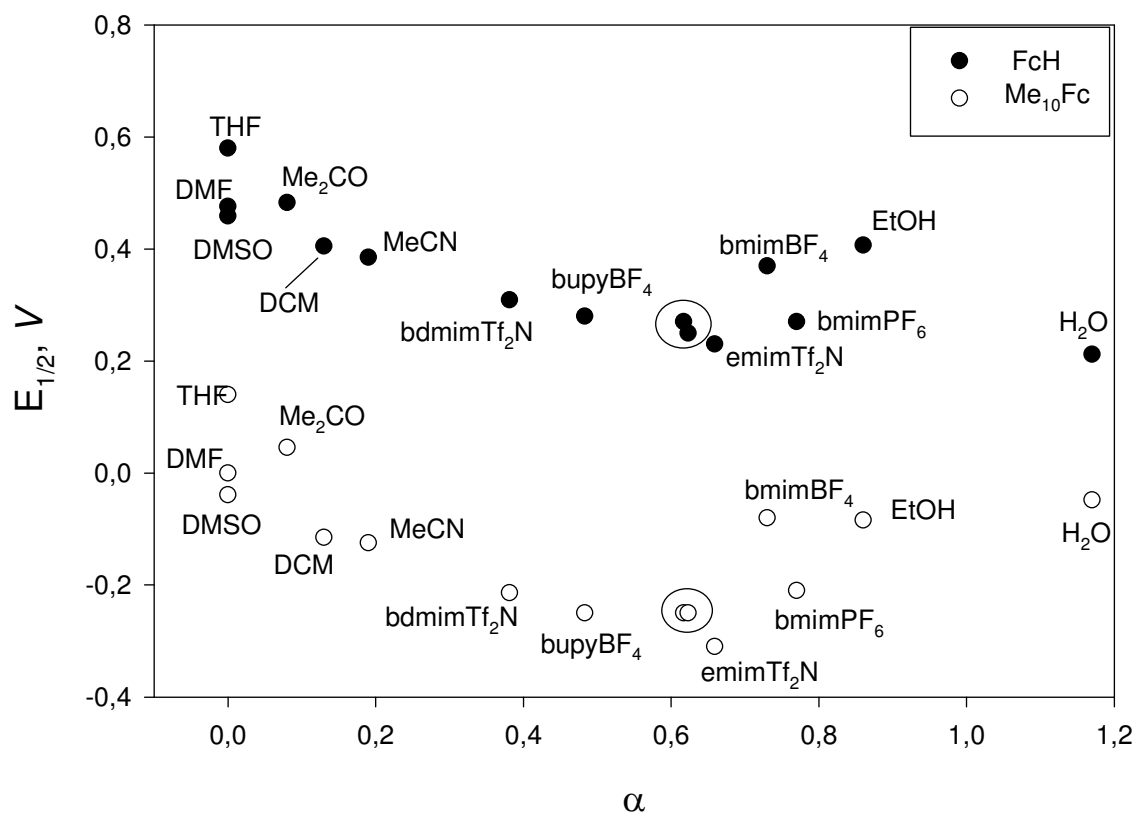
SOLVENT EFFECTS OF IONIC LIQUIDS: INVESTIGATION OF FERROCENES AS ELECTROCHEMICAL PROBES

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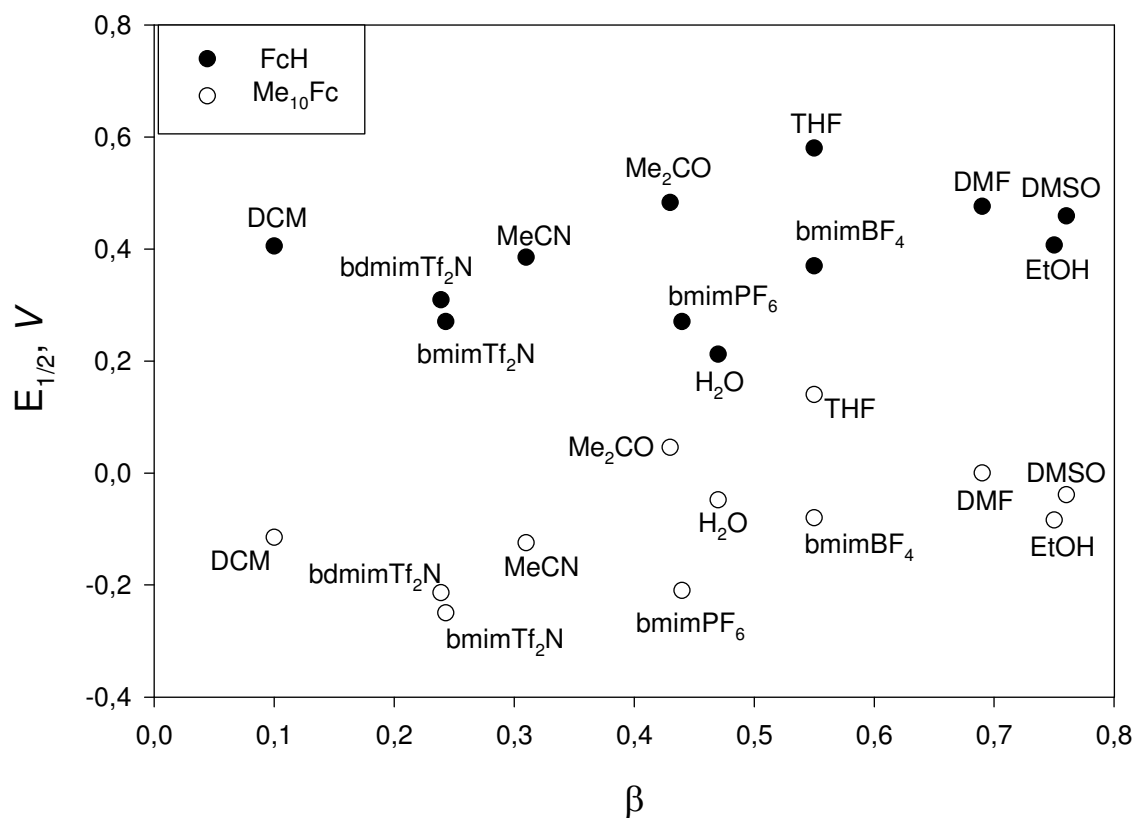
SUPPORTING INFORMATION



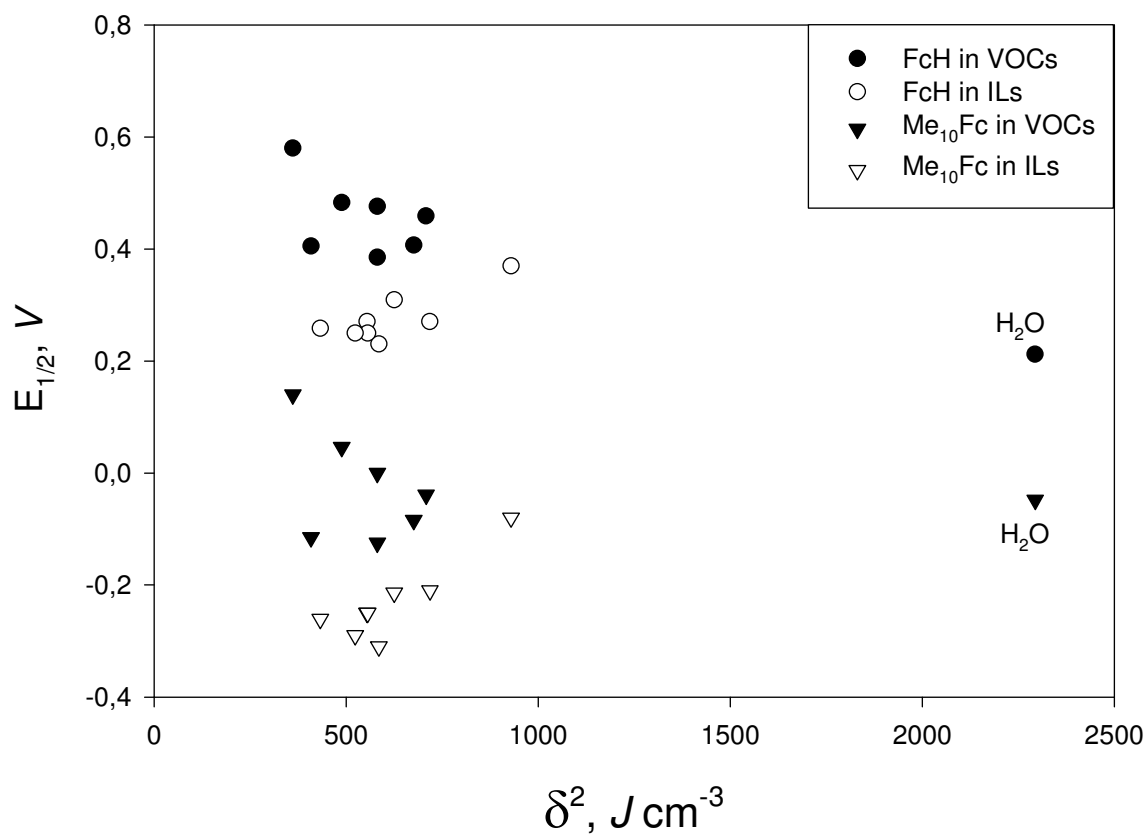
**Figure S1.** Redox potentials of ferrocene (FcH) and decamethylferrocene ( $\text{Me}_{10}\text{Fc}$ ) vs.  $\pi^*$  values of molecular solvents and ionic liquids; in the circles: emimTf<sub>2</sub>N, bmimTf<sub>2</sub>N, hminTf<sub>2</sub>N.



**Figure S2.** Redox potentials of ferrocene (FcH) and decamethylferrocene ( $\text{Me}_{10}\text{Fc}$ ) vs.  $\alpha$  values of molecular solvents and ionic liquids; in the circles: bmimTf<sub>2</sub>N, hminTf<sub>2</sub>N.



**Figure S3.** Redox potentials of ferrocene (FcH) and decamethylferrocene (Me<sub>10</sub>Fc) vs.  $\beta$  values of molecular solvents and ionic liquids.



**Figure S4** . Redox potentials of ferrocene (FcH) and decamethylferrocene ( $\text{Me}_{10}\text{Fc}$ ) vs.  $\delta^2$  values of molecular solvents and ionic liquids.