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Original scientific paper

Electrochemical reversibility of Me$_6$Fc/Me$_6$Fc$^+$PF$_6^-$ and Me$_8$Fc/Me$_8$Fc$^+$PF$_6^-$ redox systems in acetonitrile

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Abstract

Two new redox systems, sym. 1,2,4,1′,2′,4′-hexamethylferrocene/cation sym. 1,2,4,1′,2′,4′-hexamethylferricinium and sym. octamethylferrocene/cation sym. octamethylferricinium (Me$_n$Fc/Me$_n$Fc$^+$, n = 6, 8) were studied by the cyclic voltammetry method. The observed difference between potentials of anodic and cathodic peaks of 0.063 to 0.075 V, and its independence on the potential scan rate, the straight-line dependence of the current value of anodic (and cathodic) peak on square root of the potential scan rate, as well as shapes of the recorded cyclic voltammograms indicate that both redox systems in acetonitrile meet the most important requirement of IUPAC regarding internal reference redox systems (IRRS) - electrochemical reversibility of electron transfer reaction. The same method under identical conditions was used to study the effect of the number of methyl groups on the redox potential of Me$_n$Fc/Me$_n$Fc$^+$ systems, n = 0, 6, 8, 10. It was shown that the successive displacement of half-wave potential in the series of Fc/Fc$^+$ $\rightarrow$ Me$_6$Fc/Me$_6$Fc$^+$ $\rightarrow$ Me$_8$Fc/Me$_8$Fc$^+$ $\rightarrow$ $\rightarrow$ Me$_{10}$Fc/Me$_{10}$Fc$^+$ towards negative potentials is attributed to the electron-donor property of methyl groups. The location of the redox potentials values of new systems [n=6 (111 mV), n=8 (23 mV)] between redox potentials of systems of n = 0 (431 mV) and n = 10 (-77 mV) means that the redox potential of the systems of Me$_n$Fc/Me$_n$Fc$^+$(n = 6, 8) has an optimal position on the electrode potential scale, i.e. meets another of the IUPAC criteria for IRRS.

Keywords

Internal reference redox systems; voltammetry; sym. hexamethylferrocene; sym. hexamethylferricinium; sym. octamethylferrocene; sym. octamethylferricinium.

Introduction

Ferrocene and its derivatives are, from the point of view of internal reference redox systems (IRRS) in non-aqueous media, one of the most widely studied chemical materials over the past

10-15 years [1,2]. Currently for this purpose, the ferrocene-ferricinium system is commonly used [1,3]. Periodic reports on its instability [4,5], however, have initiated numerous researches to find, from the point of view of the IUPAC criteria [1,6], more promising systems consisting of methyl homologues of ferrocene and ferricinium cation [7,8].

An advantage of Me_nFc/Me_nFc^+ (n = 6, 8, 10) systems in comparison with the Fc/Fc^+ system arises from the fact that the potential of Me_nFc/Me_nFc^+ (n = 6, 8, 10) systems depends to a lesser extent on the nature of the solvent than the potential of Fc/Fc^+ system. This feature of Me_nFc/Me_nFc^+ (n = 6, 8, 10) redox systems is due to electron-donor properties and spatial dimensions of methyl groups. On the one hand, electron-donor properties of methyl groups partially compensate for a positive charge on the iron atom. On the other hand, emergence of several Me groups in cyclopentadienyl rings noticeably increases spatial dimensions (volume) of the polymethylcyclopentadienyl ring. Both factors will weaken the interaction of solvent molecules both with the central iron atom and aromatic ring of the reagents (Me_nFc and Me_nFc^+). Therefore, the potential of the Me_nFc/Me_nFc^+ (n = 6, 8, 10) redox systems is less affected by the solvent than the potential of the Fc/Fc^+ system.

Among IUPAC criteria, the most important is the reversibility of the electron transfer reaction proceeding with the participation of the redox system (eq. 1):

$$Me_nFc \leftrightarrow Me_nFc^+ + e^- \text{ (n = 6, 8)} \tag{1}$$

In our previous work [9] the reversibility of the electron exchange in two redox systems, Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+ was evidenced by the ^1H NMR method.

The purpose of this work is to define the electrochemical reversibility of the electron transfer reaction proceeding in the redox systems Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+ by the method of cyclic voltammetry.

Experimental

Electrochemical study of redox system of Me_nFc/Me_nFc^+ (n = 6, 8) was conducted in a three-electrode cell using the potentiostat of IVIUMSTAT Electrochemical Interface. As the working electrode, a platinum wire was used, platinum plate served as the auxiliary electrode, while silver/silver chloride electrode (Ag/AgCl in acetonitrile, 0.1 M $[NBu_4][PF_6]$) was used as the reference electrode. The reference electrode was isolated from the cell solution with the Luggin's capillary, filled with the buffer solution (hexafluorophosphate tetrabutylammonium ($[NBu_4][PF_6]$), 0.1 M). The concentration of the reagent (Me_nFc) in the solution was 1 mM.

As an electrolyte, hexafluorophosphate tetrabutylammonium ($[NBu_4][PF_6]$) (Sigma-Aldrich) was used. Before using, the salt was dried during an hour at the temperature of 105 °C by a vacuum pump [3]. The cyclic voltammograms were recorded in the presence of 0.1 M $[NBu_4][PF_6]$ in acetonitrile purified from oxygen and traces of water, in the argon atmosphere. Temperature of the system was kept constant ($\pm$0.1 K) by a thermostat.

Neutral complexes Me_6Fc and Me_8Fc were subliminated at temperature of 40 and 60 °C under the pressure of 0.01 MPa, and recrystallized twice from hexane solution. The salts $Me_nFc^+PF_6^-$ (n = 6, 8) in the form of acetone solution passed through a column with an aluminum oxide with height of 3 - 4 cm and recrystallized twice from a mixture of acetone with hexane.

Results and discussion

In Figure 1, cyclic voltammograms recorded for the systems of Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+, recorded at various scan rates of potential, ν = 0.02, 0.05, 0.1, and 0.2 V s^{-1}, are shown.

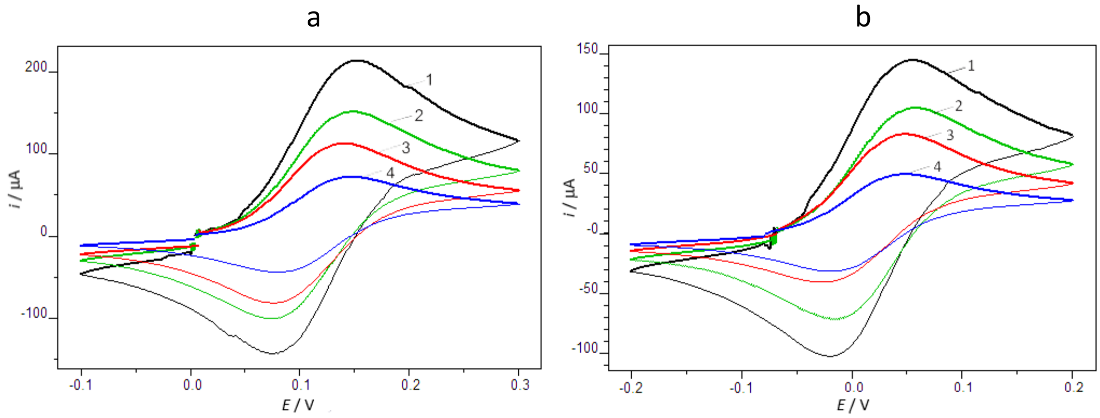

Figure 1. *Cyclic voltammograms of redox systems Me_6Fc/Me_6Fc^+ (a), and Me_8Fc/Me_8Fc^+ (b) in electrolyte solution (supporting electrolyte: $[NBu_4][PF_6]$ (0.1M), solvent: acetonitrile, concentration of Me_6Fc, Me_8Fc - 1 mM, scan rate: 1- 0.2 V s^{-1}; 2 - 0.1 V s^{-1}; 3 - 0.05 V s^{-1}; 4 - 0.02 V s^{-1}*

The characteristics of cyclic voltammograms of the studied redox systems are described in Table 1.

Table 1*. The characteristics of cyclic voltammograms of the redox systems of Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+*

ν / V s^{-1}	E_{pa} / V*	E_{pc} / V	ΔE_p / V	$E_{1/2}$ / V
		Me_6Fc/Me_6Fc^+		
0.02	0.136	0.067	0.069	0.102
0.05	0.142	0.071	0.071	0.107
0.10	0.147	0.074	0.073	0.111
0.20	0.151	0.076	0.075	0.113
		Me_8Fc/Me_8Fc^+		
0.02	0.054	– 0.009	0.063	0.022
0.05	0.055	– 0.010	0.065	0.023
0.10	0.057	– 0.010	0.067	0.023
0.20	0.058	– 0.011	0.069	0.024

*Potentials were calculated relatively to acetonitrile solution of silver chloride (Ag/AgCl) reference electrode (buffer solution – 0.1 M $[NBu_4][PF_6]$)

Here ν is the scan rate of the potential, E_{pa} – anodic peak potential, E_{pc} – cathodic peak potential, i_{pa}/i_{pc} is the ratio of the anodic and cathodic peak current, ΔE_p is difference of potentials of anodic and cathodic peaks (E_{pa} - E_{pc}), $E_{1/2}$ is half-wave potential, $(E_{pa} + E_{pc})/2$.

Consideration of parameters presented in Table 1 and corresponding cyclic voltammograms allow distinguishing three general features of voltammograms that confirm reversibility of the redox reactions of Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+:

1. the value of potential difference of the anodic and cathodic peaks (ΔE_p) is, regardless of the scan rate of the potential at 25 °C, in the range of 0.063 - 0.075V.
2. Straight-line correlation of the current value of anodic (or cathodic) peak and square root of the scan rate of the potential shown in Figure 2, supports the correspondence of both redox systems to the Randles-Ševčik equation.
3. The forms of cyclic voltammograms, as well as proximity of ratio of the anodic and cathodic peak current to the unit (0.92 - 1.15).

Above mentioned features of voltammograms allow us to make the conclusion that the heterogeneous reaction of the electron transfer in the redox systems of Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+ is the one-electron reversible process.

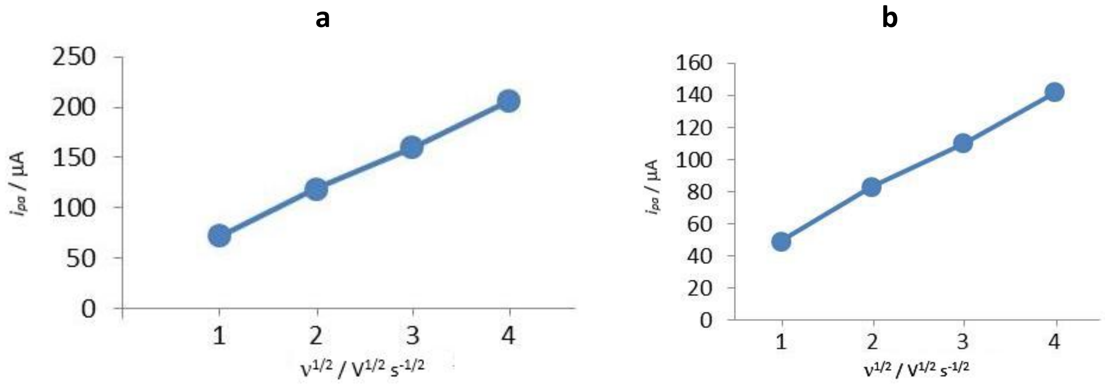

***Figure 2.** Linear dependence of anodic peak current values and square root of potential scan rate for redox systems Me_6Fc/Me_6Fc^+ (a) and Me_8Fc/Me_8Fc^+ (b)*

The main point of this conclusion is that Me_nFc/Me_nFc^+ (n = 6, 8) systems are quite stable in acetonitrile during electrochemical studies, whereas the data obtained from the cyclic voltammograms indicate the absence of the side chemical reactions in the system. Therefore the systems of Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+ showing the electrochemical reversibility in organic solvent (acetonitrile) can be used for the development of the reversible IRRS in non-aqueous media.

Similar conclusion on stability of these two systems in other organic solvents and their mixtures with water was defined in the work on study of kinetics of the electron exchange reaction in homogeneous systems Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+ by the method of ^1H NMR [9].

In Table 2, the half-wave potential value ($E_{1/2}$) of redox systems Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+, along with the values $E_{1/2}$ for the redox system of Fc/Fc^+ and $Me_{10}Fc/Me_{10}Fc^+$ are shown. The values of the half-wave potential for Fc/Fc^+ and $Me_{10}Fc/Me_{10}Fc^+$ [1,10] were obtained from our voltammetric studies conducted under identical conditions as for the systems of Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+.

***Table 2**. The half-wave potential values for Me_nFc/Me_nFc^+ (n=0,6,8,10) redox systems (ν = 0.1 V s^{-1})*

Redox system	Fc/Fc^+	Me_6Fc/Me_6Fc^+	Me_8Fc/Me_8Fc^+	$Me_{10}Fc/Me_{10}Fc^+$
$E_{1/2}$ / mV	431	111	23	– 77

It is seen from Table 2 that half-wave potential values of Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+ redox systems are in the scale of electrode potentials located approximately in the same region as $E_{1/2}$ of Fc/Fc^+ and $Me_{10}Fc/Me_{10}Fc^+$ redox systems which were recommended as IRRS in non-aqueous media [3].

The electrochemical reversibility of Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+ redox systems in an organic solvent (acetonitrile), and the optimal range of location of their redox potentials indicate the necessity of the further study on establishing the correspondence of these systems (n = 6, 8) with remaining criteria for the reference electrode [1,6]. Currently, we are continuing electrochemical studies of these two systems in various organic solvents, ionic liquids, and mixtures of organic solvent/water.

It is also seen from Table 2 that in the series of $Me_6Fc/Me_6Fc^+ \rightarrow Me_8Fc/Me_8Fc^+ \rightarrow$ $\rightarrow Me_{10}Fc/Me_{10}Fc^+$, $E_{1/2}$ of the subsequent redox system consistently shifts towards negative potentials. The shift for the system of Me_8Fc/Me_8Fc^+ relatively to Me_6Fc/Me_6Fc^+ is 87 mV, but for the system of $Me_{10}Fc/Me_{10}Fc^+$ relatively to Me_8Fc/Me_8Fc^+ is 101 mV. These suggest that appearing of two additional methyl groups in the composition of each reagent causes the shift of the half-wave potential for 90–100 mV in the direction of negative potential.

The observed shifts of $E_{1/2}$ in the series of $Fc/Fc^+ \rightarrow Me_6Fc/Me_6Fc^+ \rightarrow Me_8Fc/Me_8Fc^+ \rightarrow$ $\rightarrow Me_{10}Fc/Me_{10}Fc^+$ should be attributed to the electron-donor property of the methyl groups which facilitates one-electron oxidation of the corresponding neutral polymethylferrocene. Indeed, a comparative study of photoelectron spectra of ferrocene and decamethylferrocene [11] showed that the ionization potential of d-electron of iron atom in decamethylferrocene is approximately 1.0 eV less than the corresponding ionization potential in the ferrocene molecule. Moreover, as in the sequence $Me_6Fc/Me_6Fc^+ \rightarrow Me_8Fc/Me_8Fc^+ \rightarrow Me_{10}Fc/Me_{10}Fc^+$, in the series of $Fc/Fc^+ \rightarrow Me_2Fc/Me_2Fc^+ \rightarrow \ldots \rightarrow Me_{10}Fc/Me_{10}Fc^+$, the electron effect of methyl groups has an additive character: in case of decreasing ionization potential of d-electron of 1,1′-dimethylferocene in comparison with ionization potential of ferrocene it is equal to 0.2 eV, then this value is 5 times higher for decamethylferrocene and it is 1 eV, as noted above.

Conclusion

It was shown by cyclic voltammetry method that the electron transfer reaction of redox systems Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+ in an organic solvent (acetonitrile) is a reversible one. The range of their redox potential is in the optimal region of electrode potential scale. This means that the systems of Me_6Fc/Me_6Fc^+ and Me_8Fc/Me_8Fc^+ meet two of seven criteria of IUPAC postulated for an IRRS in non-aqueous media. Therefore, further studies of these systems as internal reference redox systems are required.

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