The Observation of Ion-Pairing Effect based on Substituent Effect of Ferrocene Derivatives

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Abstract

The ion-pairing effect was investigated based on the substituent effect of ferrocene (Fc) derivatives using cyclic voltammetry. It was shown that the presence of ion-pairing strongly affected the electrochemical redox behavior in the organic solvent. The formal redox potential ($E^{0'}$, the average of anodic and cathodic peak potential) shifted negatively with the increasing ion-pairing effect. That was because the formation of ion pair ($\text{Fc}^+ \cdot \text{ClO}_4^-$) was beneficial to equilibrium shift from Fc to Fc^+ in thermodynamics. In this work, electron-donating and electron-withdrawing substituents of ferrocene derivatives were employed for deep study of ion-pairing effect, respectively. It is confirmed that both ion-pairing effect and electron-donating substituent effect facilitated the negative shift of $E^{0'}$ for ferrocene derivatives, showing the positive cooperativity. While the electron-withdrawing substituent effect resulted in the positive shift of $E^{0'}$ for ferrocene derivatives and was unfavourable for

the oxidation of Fc derivatives, reflecting the negative cooperativity with ion-pairing effect. In addition, the reversal phenomenon of weak electron-withdrawing substituent was revealed when the ion-pairing effect was stronger than the electron-withdrawing substituent effect, indicating the ion-pairing function has a significant effect on electrochemical behavior of ferrocene derivatives.

Keywords: Ferrocene derivatives; Substituent effect; Ion-pairing effect; Positive/Negative cooperativity; Reversal phenomenon

1. Introduction

Ferrocene (Fc) and its derivatives attract extensive research interest largely due to their inherent reversible redox property, excellent thermal stability and good solubility in non-aqueous solvent. Many ferrocene derivatives have been synthesized and studied [1-5] for diverse applications in functional material science [6-9], biological chemistry and electrochemistry [10-13]. Among them, one of the most noticeable features is the favorable redox properties of Fc, which makes it a popular marker in electrochemical biosensors [14-16].

The oxidation of neutral Fc generates the oxidized ferrocenium cation (Fc^+), which forms ion-pairing with anions in solution. Thus, the redox reaction of Fc is influenced by the presence of anions in the medium [17-21]. The ability to form ion pairs with Fc^+ varies for the different type and concentration of anions. Consequently, the voltammetric behavior (including formal redox potential and peak shapes) of Fc is

strongly influenced by ion-pairing effect. There are a few reports in the literature that provides considerable insight into the fundamentally important aspect for ion-pairing effect on electrochemical behavior of ferrocene derivatives. The effects of the nature and concentration of counter anions in aqueous media on cyclic voltammetry (CV) was investigated in a polymer film by Inzelt and Szabo [20]. Subsequently, the ion-pairing effect on the redox behavior of Fc was studied in self-assembled monolayers (SAMs) [22,23]. Uosaki and co-workers performed CV of the ferrocenyl SAMs in various concentrations of HClO₄ solutions and proposed that the shape and position of the redox peaks were strongly affected by the anion [22]. In a later research, Kondo et al. studied the ion-pair formation between Fc⁺ and different anions in the aqueous and dichloromethane solutions and discovered an opposite tendency in the two phases [23]. In our previous work done by Xiang [24-26], the redox behavior and ion-pairing thermodynamics of ferrocenyl compounds in the organic phase have been studied. It showed that the presence of supporting electrolytes in the organic phase complicated their redox behavior. Although it is interesting and important to investigate the ion-pairing effect of ferrocene derivatives in organic solvents for fundamental science and industrial applications, few reports are available on the ion-pairing effect based on substituent effect of ferrocene derivatives.

In this work, we have studied the ion-pairing effect based on the electron-donating and electron-withdrawing substituents of ferrocene derivatives, respectively. It presents both the positive and negative cooperativity between substituent effect and ion-pairing effect. Reversal phenomenon of weak

electron-withdrawing substituent on redox potentials is confirmed. The work is conducive to achieve a better understanding for the ion-pairing effect on electrochemical behavior of ferrocenyl derivatives.

2. Experimental

2.1. Chemical reagents

Ferrocene (Fc), aminoferrocene (described as Fc-NH₂), ferrocenylmethanol (described as Fc-CH₂OH), bromoferrocene (described as Fc-Br), ferrocenecarboxaldehyde (described as Fc-CHO), vinyl ferrocene (described as Fc-CH=CH₂), 1,2-dichloroethane (DCE), tetraethylammonium perchlorate (TEAP) and 1-ethyl-3-methylimidazolium hexafluorophosphate ([Emim]PF₆) were purchased from a chemical supplier (J&K Scientific Co., Ltd., Beijing, China). All chemicals were of analytical grade or better and used as received without further purification. The used ultrapure water with 18.2 MΩ·cm was from a Milli-Q filter (Research UV, Hetai Instrument Co. Ltd., Shanghai, China).

2.2. Apparatus and Procedure

Electrochemical measurements were performed in a conventional three-electrode cell. Gold (Au) disk as working electrode (3 mm in diameter), platinum wire as counter electrode and Ag|Ag⁺ (0.01 M AgNO₃ in DCE, saturated [Emim]PF₆) as reference electrode were purchased from CH Instrument (Chenhua Instrument Co., Ltd., Shanghai, China). Before measurement, the working electrode was mechanically

polished with 1.0, 0.3 and 0.05 μm alumina slurries in particle size successively. After polishing, the working electrode was sonicated for 5 min in a 1:1 v/v mixture of water and ethanol. Then the working electrode was potentiostatically scanned (100 mV s^{-1}) for 30 cycles in 1.0 M sulfuric acid solution with the potential window from -0.2 to 1.6 V (vs. SCE) and dried in the nitrogen atmosphere for 10 min. Fc and its ferrocene derivatives were dissolved in DCE containing 0.1 M [Emim]PF₆, respectively. All solutions were bubbled with nitrogen for 10 min. CV was performed using a potentiostat (CHI 920C, Chenhua Instrument Co. Ltd., Shanghai, China). All potentials were reported against the Ag|Ag⁺.

3. Result and Discussion

3.1. Ion-pairing effect based on electron-donating substituent

In this study, aminoferrocene (described as Fc-NH₂) and ferrocenylmethanol (described as Fc-CH₂OH) were selected as strong and weak electron-donating substituent for investigating ion-pairing effect, respectively. In our experiments, the formal redox potential ($E^{0'}$, the average of anodic and cathodic peak potential) of 1mM Fc (without ClO₄⁻) was used as a reference, aiming to compare the shift of $E^{0'}$ for ferrocene derivatives (absence or presence of ClO₄⁻ in solution). 0.1 M [Emim]PF₆ was used as the supporting electrolyte.

As shown in Fig. 1A and 1B, pairs of well-shaped redox peaks of Fc⁺/Fc were observed at the Au electrode. The anodic peak currents (I_{pa}) and cathodic peak currents (I_{pc}) were nearly identical for each voltammogram, indicating that

oxidation-reduction reaction was chemically reversible.

In this work, the TEAP was added into the systems for studying the ion-pairing effect based on electron-donating substituent of ferrocene derivatives. Although the PF_6^- anion had similar ion-pairing ability as ClO_4^- [21] as supporting electrolyte, we fixed the concentration of PF_6^- (0.1 M) throughout the experiment by control over the presence or absence of ClO_4^- and different substituents. Hence, ion-pairing effect caused by $\text{Fc}^+\cdot\text{ClO}_4^-$ is the main influence factors. The redox reaction should be expressed as follows:

Instead of a simple one-electron reversible process and the ion-pair formation, it can be considered as follows.

The relevant electrochemical data of Fc and its derivatives were listed in Table 1. One clear trend was seen in Table 1 and Fig.1, the $E^{0'}$ of Fc (within ClO_4^-) (0.153 V in Fig. 1A(b)) shifted 30 mV cathodically compared with Fc (0.183 V in Fig. 1A(a)). It was attributed to the ion-pairing effect of $\text{Fc}^+\cdot\text{ClO}_4^-$. The formation of ion pair ($\text{Fc}^+\cdot\text{ClO}_4^-$) was beneficial to the equilibrium shift from Fc to Fc^+ (eq.(2)). It facilitated the oxidation of Fc.

Fc-NH_2 was employed as ferrocene derivative with strong electron-donating substituent. Inspection of Fig.1A and Table 1 revealed that the $E^{0'}$ of Fc-NH_2 (-0.159 V in Fig. 1A(c)) shifted 342 mV negatively compared with Fc (0.183 V in Fig. 1A(a)),

owing to electron-donating substituent effect. It promoted the negative shift of $E^{0'}$ for ferrocene derivatives and was conducive to the oxidation of Fc-NH₂. It was interpreted as the following factor: the electron-donating substituent resulted in the increase of electron density on iron atom and the energies of HOMO (Highest Occupied Molecular Orbital).

With the addition of TEAP, the $E^{0'}$ of Fc-NH₂ (within ClO₄⁻) (-0.195 V in Fig. 1A(d)) shifted 378 mV cathodically compared with Fc (0.183 V in Fig. 1A(a)). The more negative shift for the $E^{0'}$ of Fc-NH₂ (Fig. 1A(d)) reflected two effects: ion-pairing effect and electron-donating substituent effect. Both ion-pairing effect and electron-donating substituent effect facilitated the negative shift of $E^{0'}$ for Fc-NH₂. In addition, the negative shift (Fig. 1A(d)) was more than that two superimposition effect (378 mV > 30 mV + 342 mV). The result showed the positive cooperativity between ion-pairing effect and electron-donating substituent effect.

Analogously, the $E^{0'}$ of Fc (within ClO₄⁻) (0.153 V in Fig. 1B(b)) shifted 30 mV cathodically compared with Fc (0.183 V in Fig. 1B(a)). For ferrocene derivative with weak electron-donating substituent, the $E^{0'}$ of Fc-CH₂OH (0.192 V in Fig. 1B(c)) showed a negligible positively shift of 9 mV compared with Fc (0.183 V in Fig. 1B(a)) on account of the combined effects including weak hyperconjugation effect and steric hindrance of -CH₂OH. While the $E^{0'}$ of Fc-CH₂OH (within ClO₄⁻) (0.155 V in Fig. 1B(d)) shifted 28 mV negatively compared with Fc (0.183 V in Fig. 1B(a)). The negative shift for the $E^{0'}$ of Fc-CH₂OH also reflected the positive cooperativity (28 mV > 30 mV - 9 mV). Thus it can be seen that the positive cooperativity was

available, regardless of strong and weak electron-donating substituent.

Moreover, the ΔE_p (peak-to-peak potential separation) of Fc-NH₂ decreased from 113 (Fig. 1A(c)) to 85 mV (Fig. 1A(d)), showing the faster electron-transfer kinetics between Fc-NH₂ and electrode in the presence of ClO₄⁻. The present positive cooperativity and decreased ΔE_p indicated the significance of ion-pairing studies based on electron-donating substituent.

Taking Fc-NH₂ as an example, Fig. 2 showed the CVs at different scan rates. It was evident that the CVs still remained well-shaped and reversible redox peaks in the range from 50 to 300 mV s⁻¹. Moreover, peak current increased with the increase of the scan rates, while the $E^{0'}$ of Fc-NH₂ (within ClO₄⁻) remained nearly unchanged. It exhibited reversible electrochemical redox for ferrocenyl compounds. Inset of Fig. 2 showed a linear relation between I_{pa} and the square root of the scan rate ($v^{1/2}$) in Fc-NH₂. The linear relationship suggested that the reaction was a diffusion-controlled process.

3.2. Ion-pairing effect based on electron-withdrawing substituent

In contrast, bromoferrocene (described as Fc-Br) and ferrocenecarboxaldehyde (described as Fc-CHO) were employed for studying the ion-pairing based on electron-withdrawing substituent of ferrocene derivatives. Fig. 3 showed CVs of Fc and its derivatives in the presence or absence of ClO₄⁻ in solution. As follows in Table 2, the $E^{0'}$ of Fc (within ClO₄⁻) (0.153 V in Fig. 3A(b)) shifted 30 mV negatively compared with Fc (0.183 V in Fig. 3A(a)) after adding TEAP. This explanation had

been elaborated above. Introducing electron-withdrawing substituent, the $E^{0'}$ of Fc-Br (0.355 V in Fig. 3A(c)) shifted 172 mV positively compared with Fc (0.183 V in Fig. 3A(a)). The reason was that the electron-withdrawing substituent increased positive charge of iron atoms and reduced the energies of HOMO, so it was unfavourable for the oxidation of Fc derivatives [27].

The addition of TEAP and ferrocene derivative with electron-withdrawing substituent, the $E^{0'}$ of Fc-Br (within ClO_4^-) (0.333 V in Fig. 3A(d)) shifted 150 mV positively compared with Fc (0.183 V in Fig. 3A(a)). The less positive shift of Fc-Br (150 mV < 172 mV) was due to the ion pairing effect based on the electron-withdrawing substituent. The ion pairing effect resulted in the negative shift of the $E^{0'}$ for Fc-Br, which was opposite to the electron-withdrawing substituent effect, showing the negative cooperativity.

Similarly for Fc-CHO, the $E^{0'}$ of Fc-CHO (0.486 V in Fig. 3B(c)) shifted 303 mV positively compared with Fc (0.183 V in Fig. 3B(a)). While the $E^{0'}$ of Fc-CHO (within ClO_4^-) (0.454 V in Fig. 3B(d)) shifted 271 mV positively compared with Fc (0.183 V in Fig. 3B(a)). It also showed negative cooperativity between ion-pairing effect and electron-withdrawing substituent effect.

In this system, although the ion pair was introduced, the $E^{0'}$ of Fc-Br (within ClO_4^-) (0.333 V in Fig. 3A(d)) and Fc-CHO (within ClO_4^-) (0.454 V in Fig. 3B(d)) were still more positive than the Fc (0.183 V in Fig. 3A(a)). It indicated that the electron-withdrawing substituent effect was far stronger than ion-pairing effect. Furthermore, the extent of positive shift was gradually increased with the enhanced

electron-withdrawing effect ($\text{Fc-CHO} > \text{Fc-Br}$).

3.3. Reversal phenomenon of weak electron-withdrawing substituent on electrochemical behaviour

In the above-mentioned experiments, we studied ion-pairing effect based on electron-donating and electron-withdrawing substituents of ferrocene derivatives, respectively. The results showed that ion-pairing effect exerted an influence on electrochemical behavior of ferrocene derivatives, showing positive and negative cooperativity, respectively. In the negative cooperativity, when ion-pairing effect was stronger than the weak electron-withdrawing substituent effect, reversal phenomenon of the ferrocene derivatives was observed. Hence, vinyl ferrocene (described as Fc-CH=CH_2) was selected as ferrocene derivative with weak electron-withdrawing substituent to explore the reversal phenomenon.

As a demonstration, Fig. 4 clearly showed that the $E^{0'}$ of Fc-CH=CH_2 (0.198 V in Fig. 4(b)) shifted 15 mV positively in contrast to Fc (0.183 V in Fig. 4(a)) on account of weak electron-withdrawing substituent effect. While the $E^{0'}$ of Fc-CH=CH_2 (within ClO_4^-) (0.173 V in Fig. 4(c)) shifted 10 mV negatively in contrast to Fc (0.183 V in Fig. 4(a)) because of ion-pairing effect. It was different from the strong electron-withdrawing substituents. In this case, ion-pairing effect was stronger than the weak electron-withdrawing substituent effect, so the $E^{0'}$ of Fc-CH=CH_2 (within ClO_4^-) was more negative than the $E^{0'}$ of Fc.

Different concentrations of counter anions (within ClO_4^-) lead to the variations of

the observed $E^{0'}$ [22] and the reversal phenomenon without exception. Fig. 5 showed CVs of Fc-CH=CH₂ at different concentrations of ClO₄⁻, respectively. The negative shift of anodic peak potential became more obvious with the increase of concentration. The linear regression equation was expressed by $E_{pa} = 0.200 \text{ (V)} - 0.0198 \log[\text{ClO}_4^-]$ (inset of Fig. 5). In the range from 0 to 0.02 M, slightly negative shift of anodic peak potential occurred and reversal phenomenon was not observed. It was explained that the ion-pairing effect was weak in the range of low concentration and not enough to offset electron-withdrawing effect. With the increase of ClO₄⁻ concentration (from 0.02 to 0.13 M), the reversal phenomenon became more and more obvious. All these results demonstrated that ion-pairing effect played a significant influence on electrochemical behavior of ferrocene derivatives.

4. Conclusion

This work investigated the ion-pairing effect based on the electron-donating and electron-withdrawing substituents effect, respectively. The shift of $E^{0'}$ for ferrocene derivatives was used to estimate the positive cooperativity and negative cooperativity between ion-pairing effect and substituent effect, respectively. The formation of ion pair caused the negative shift of $E^{0'}$ for ferrocene derivatives. It attributed to the fact that the formation of ion pair (Fc⁺•ClO₄⁻) promoted the equilibrium to move towards the oxidation of Fc. It benefited the oxidation of Fc. Both ion pairing effect and electron-donating effect facilitated the negative shift of $E^{0'}$ for ferrocene derivatives, showing the positive cooperativity. While electron-withdrawing substituent effect

resulted in the positive shift of $E^{0'}$ for ferrocene derivatives, which was opposite to the ion pairing effect, reflecting the negative cooperativity with ion-pairing effect. Besides, the reversal phenomenon was observed when ion-pairing effect was far stronger than weak electron-withdrawing substituent effect. This work will attract more attention to the significant aspect of ion-pairing effect on electrochemical behavior of ferrocene derivatives and the beyond.

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Figure Captions:

Fig.1. (A) CVs of 1 mM Fc (a(—)), 1 mM Fc and 0.1 M TEAP (b(— — —)), 1 mM Fc-NH₂ (c(— · —)), 1 mM Fc-NH₂ and 0.1 M TEAP (d(·····)). (B) CVs of 1 mM Fc (a(—)), 1 mM Fc and 0.1 M TEAP (b(— — —)), 1 mM Fc-CH₂OH (c(— · —)), 1 mM Fc-CH₂OH and 0.1 M TEAP (d(·····)). Scan rate was 50 mV s⁻¹.

Fig. 2. CVs of 1 mM Fc-NH₂ containing 0.1 M TEAP at different scan rates: 50, 100, 150, 200, 300 mV s⁻¹ (from inner to outer), respectively. Inset: the plots of I_{pa} vs. $v^{1/2}$.

Fig. 3. (A) CVs of 1 mM Fc (a(—)), 1 mM Fc and 0.1 M TEAP (b(— — —)), 1 mM Fc-Br (c(— · —)), 1 mM Fc-Br and 0.1 M TEAP (d(·····)). (B) CVs of 1 mM Fc (a(—)), 1 mM Fc and 0.1 M TEAP (b(— — —)), 1 mM Fc-CHO (c(— · —)), 1 mM Fc-CHO and 0.1 M TEAP (d(·····)). Scan rate was 50 mV s⁻¹.

Fig.4. CVs of 1 mM Fc (a(—)), 1 mM Fc-CH=CH₂ (b(— — —)), 1 mM Fc-CH=CH₂ and 0.1 M TEAP (c(— · —)). Scan rate was 50 mV s⁻¹.

Fig.5. CVs of 1 mM Fc-CH=CH₂ and different concentrations of counter anions ClO₄⁻: 0 M (a(—)), 0.005 M (b(— — —)), 0.05 M (c(— · —)), 0.10 M (d(···)), 0.13 M (e(— · — ·)), respectively. Inset: the plots of E_{pa} vs. log [ClO₄⁻].

Table 1

Electrochemical data based on electron-donating substituent of ferrocene derivatives.

Compound	$I_{pa}/\mu A$	$I_{pc}/\mu A$	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$E^{0'}/V$
Fc	6.537	6.005	0.242	0.124	0.118	0.183
Fc (ClO ₄ ⁻)	5.760	6.317	0.196	0.109	0.087	0.153
Fc-NH ₂	4.736	4.612	-0.102	-0.215	0.113	-0.159
Fc-NH ₂ (ClO ₄ ⁻)	4.767	4.926	-0.152	-0.237	0.085	-0.195
Fc-CH ₂ OH	4.445	4.906	0.249	0.135	0.114	0.192
Fc-CH ₂ OH (ClO ₄ ⁻)	4674	4.908	0.200	0.110	0.090	0.155

I_{pa} : anodic peak current; I_{pc} : cathodic peak current; E_{pa} : anodic peak potential; E_{pc} : cathodic peak potential; ΔE_p : peak-to-peak potential separation; $E^{0'}$: formal redox potential. All potentials were reported against the Ag|Ag⁺.

Table 2

Electrochemical data based on electron-withdrawing substituent of ferrocene derivatives.

Compound	$I_{pa}/\mu A$	$I_{pc}/\mu A$	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$E^{0'}/V$
Fc	6.537	6.005	0.242	0.124	0.118	0.183
Fc (ClO ₄ ⁻)	5.760	6.317	0.196	0.109	0.087	0.153
Fc-CH=CH ₂	5.912	5.953	0.254	0.141	0.113	0.198
Fc-CH=CH ₂ (ClO ₄ ⁻)	5.930	5.902	0.216	0.131	0.085	0.173
Fc-Br	6.013	5.738	0.414	0.296	0.118	0.355
Fc-Br (ClO ₄ ⁻)	5.948	6.296	0.375	0.291	0.084	0.333
Fc-CHO	5.179	5.170	0.541	0.430	0.111	0.486
Fc-CHO (ClO ₄ ⁻)	5.044	5.005	0.495	0.413	0.082	0.454

I_{pa} : anodic peak current; I_{pc} : cathodic peak current; E_{pa} : anodic peak potential; E_{pc} : cathodic peak potential; ΔE_p : peak-to-peak potential separation; $E^{0'}$: formal redox potential. All potentials were reported against the Ag|Ag⁺.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5