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ABSOLUTE ELECTROMOTIVE FORCE OF STANDARD FERROCENE-FERRICINIUM ELECTRODE IN AQUEOUS AND NON-AQUEOUS MEDIA

By

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Abstract

The absolute electromotive force of the standard Ferrocene/Ferricinium ion electrode $\varphi^{0}_{Fer/Fer^{+},s}$ where subscript s denotes solvent s has been estimated in water, acetonitrile, formamide and methanol solutions on the basis of the standard potential measured against the standard hydrogen electrode in the same solution. It has been found that $\varphi^{0}_{Fer/Fer^{+},s}$ values range from 4.82 v. in water to 4.58 v. in methanol and the difference can be attributed essentially to the difference in the surface potentials of these solvents.

Ferrocene (Fer) and ferricinium ion ($\mathbf{Fer^{+}}$) are complexes of relatively large size with $\mathbf{Fe^{2+}}$ and $\mathbf{Fe^{3+}}$ sandwitched between two cyclopentadienyl ions and the oxidized form carries only one unit of positive charge. Therefore, the interactions of ferrocene and ferricinium ion with solvent molecules can be expected to be small and essentially independent of nature of the solvent. Accordingly Strehlow[1] proposed to use the $\mathbf{Fer/Fer^{+}}$ couple as a suitable reference electrode for the comparison of the electrode potentials in different solvents in place of $\mathbf{Rb/Rb^{+}}$ couple proposed by Pleskov[2].

However, the difference of the standard potentials of $\mathbf{Fer/Fer^{+}}$ couple between in water and in dimethylformamide amounts to 0.31 v when measured against the saturated aqueous calomel electrode[3], which may be caused by the difference of the solvation free energies of ferrocene and ferricinium in the two solvents and the junction potential between water and dimethylformamide.

In the present work the absolute values of the standard electromotive force of the $\mathbf{Fer/Fer^{+}}$ electrode are estimated for some typical non-aqueous solvents as well as for water in which the standard potential of the $\mathbf{Fer/Fer^{+}}$ couple is measured against the standard hydrogen electrode. The solvation

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free energy difference between ferricinium and ferrocene in these solvents will also be discussed.

Basic formulas for estimation of absolute electromotive force

The absolute electromotive force $\varphi^{\circ}_{\mathrm{Fer/Fer^+,s}}$ of the single electrode **Fer**/**Fer**$^+$ redox system electrode in the standard state at a given temperature in a given solvents s,

$$\mathbf{Fe}\,(C_2H_5)_2 \rightleftharpoons \mathbf{Fe}\,(C_2H_5)_2^+ + e_m^- , \qquad (1)$$

may be defined as[4]

$$\varphi^{\circ}_{\mathrm{Fer/Fer^+,s}} = (\bar{\mu}^{\circ}_{e^-,g} - \bar{\mu}^{\circ}_{e^-,m})/F , \qquad (2)$$

where $\bar{\mu}^{\circ}_{e^-,g}$ and $\bar{\mu}^{\circ}_{e^-,m}$ are the electrochemical potentials of the electron in the gaseous state and in the electrode metal respectively, superscript o denotes the standard state and F is the Faraday.

The value of $\varphi^{\circ}_{\mathrm{Fer/Fer^+,s}}$ can be estimated from the standard potential of the **Fer**/**Fer**$^+$ electrode E°_s measured against the standard hydrogen electrode in the same solvent by the equation

$$\varphi^{\circ}_{\mathrm{Fer/Fer^+,s}} = E^{\circ}_s + \varphi^{\circ}_{\mathrm{H_2/H^+,s}} , \qquad (3)$$

using the absolute electromotive force of the standard hydrogen electrode $\varphi^{\circ}_{\mathrm{H_2/H^+,s}}$ in solvent s.

The value of $\varphi^{\circ}_{\mathrm{H_2/H^+,s}}$ can be estimated from the molal real free energy of solvation of the hydrogen ion $-\bar{\alpha}^{\circ}_{\mathrm{H^+,w}}$ reported by Randles in water solution[5] and from those $-\bar{\alpha}^{\circ}_{\mathrm{H^+,s}}$ in non-aqueous solvents reported by Case and Parsons[6] on the basis of the thermodynamical relation[4]

$$\Delta\mathscr{F}^{\circ}_{\mathrm{H^+,s}} = -\bar{\alpha}^{\circ}_{\mathrm{H^+,s}} + F\varphi^{\circ}_{\mathrm{H_2/H^+,s}} , \qquad (4)$$

where $\Delta\mathscr{F}^{\circ}_{\mathrm{H^+,s}}$ is the standard free energy of formation of the hydrogen ion in the gaseous state from its pure element, and $-\bar{\alpha}^{\circ}_{\mathrm{H^+,s}}$ is defined as

$$-\bar{\alpha}^{\circ}_{\mathrm{H^+,s}} = \bar{\mu}^{\circ}_{\mathrm{H^+,g}} - \bar{\mu}^{\circ}_{\mathrm{H^+,s}} . \qquad (5)$$

The absolute electromotive force of the Fer/Fer$^+$ couple and the difference of the molal real free energies of solvation between ferricinium ion and ferrocene $-\Delta\bar{\alpha}^{\circ}_s = -\bar{\alpha}^{\circ}_{\mathrm{Fer^+,s}} + \alpha^{\circ}_{\mathrm{Fer,s}}$ can also be related to the free energy of ionization I of the ferrocene molecule by the similar equation as Eq. (4)

$$I = -\Delta\bar{\alpha}^{\circ}_s + F\varphi^{\circ}_{\mathrm{Fer/Fer^+,s}} . \qquad (6)$$

The free energy of ionization of the ferrocene molecule may be given by the sum of the enthalpy and entropy change for the ionization process

of ferrocene

$$I = \Delta\overline{H}^{\circ} - T\Delta S^{\circ}, \qquad (7)$$

where $\Delta\overline{H}^{\circ}$ may be identified with the adiabatic ionization potential of the ferrocene molecule which is estimated to be 6.72 ev by the electron-spectroscopic method[7] and ΔS° is given by the entropy difference between ferricinium and ferrocene 1.4 cal/mol. deg.[8] and the entropy of the gaseous electron in the standard state 4.988 cal/mol. deg.[9]. All numerical data are referred to 25°C. In this way the value of I can be estimated to be 6.64 ev.

Absolute electromotive force of ferrocene/ferricinium electrode

The values of $\varphi^{\circ}_{\mathrm{Fer/Fer^+,s}}$ and $-\Delta\bar{\alpha}^{\circ}_{s}$ estimated in this way from the values of $-\bar{\alpha}^{\circ}_{\mathrm{H^+,s}}$, $\varphi^{\circ}_{\mathrm{H_2/H^+,s}}$ and E°_{s} are listed in Table 1 for water, acetonitrile, formamide and methanol.

TABLE 1. The absolute electromotive forces of ferrocene/ferricinium electrode and the difference of the standard molal real free energies of solvation between ferricinium and ferrocene at 25°C.

Solvent	$-\bar{\alpha}^{\circ}_{\mathrm{H^+,s}}$ (ev)	$\varphi^{\circ}_{\mathrm{H_2/H^+,s}}$ (v)	E°_{s}[10] (v)	$\varphi^{\circ}_{\mathrm{Fer/Fer^+,s}}$ (v)	$-\Delta\bar{\alpha}^{\circ}_{s}$ (ev)
water	11.30[5]	4.42	0.40	4.82	1.82
Acetonitrile	11.18[6]	4.54	0.19	4.73	1.91
Formamide	11.45[6]	4.27	0.54	4.81	1.83
methanol	11.55[6]	4.24	0.41	4.58	2.06

It can be seen from Table 1 that the values of $\varphi^{\circ}_{\mathrm{Fer/Fer^+,s}}$ ranges from 4.82 v in water to 4.58 v in methanol and the difference between the two extremum values amounts to 0.24 v, which may be regarded as a too large difference to take it for granted that the standard electromotive force of the **Fer/Fer$^+$** electrode remains constant independent of nature of the solvent. This fact should be taken into consideration in the kinetic study of electrode processes in different solvents when the **Fer/Fer$^+$** couple is used as the reference electrode.

Chemical part of solvation free energy difference between ferricinium ion and ferrocene

It is necessary to estimate the chemical part of the solvation free energy difference between ferrocene and ferricinium ion in a solvent in order to

discuss the interactions of ferrocene and ferricinium ion with the solvent molecules separately from the electrostatic effect due to the surface potential of the solvent.

We have recently estimated the chemical part of the free energy of solvation of 69 monoatomic ionic species for 15 solvents[12] on the basis of an empirical rule[4], which will enable us to estimate the chemical part of the solvation free energy difference between ferricinium ion and ferrocene $-\Delta\alpha_s^\circ$ for a series of solvents in which the E_s°-values are measured against some reference electrode. When the standard hydrogen electrode or the standard **Ag/Ag$^+$** electrode is used as the reference electrode, $-\Delta\alpha_s^\circ$ can be expressed from Eqs. (3), (4) and (6) as

$$-\Delta\alpha_s^\circ = I - \Delta\mathscr{F}_{H^+}^\circ - \alpha_{H^+,s}^\circ - E_{s(H)}^\circ , \tag{8 a}$$

or

$$-\Delta\alpha_s^\circ = I - \Delta\mathscr{F}_{Ag^+}^\circ - \alpha_{Ag^+,s}^\circ - E_{s(Ag)}^\circ \tag{8 b}$$

in which subscript (H) or (Ag) is attached to E_s° according as E_s° is measured against the standard hydrogen or **Ag/Ag$^+$** electrode. The value of $\Delta\mathscr{F}_{H^+}^\circ$ is obtained as 15.72 ev and $\Delta\mathscr{F}_{Ag^+}^\circ$ as 10.19 ev from the thermodynamical data[9]. The values of $E_{s(H)}^\circ$ are listed in Table 1. We have in the thermodynamical table[3] the values of the electromotive force of the **Fer/Fer$^+$**

TABLE 2. The chemical components of the solvation free energy difference between ferrocene and ferricinium ion at 25°C

Solvent	$E_{s(H)}^\circ$[10] (v)	$E_{s(Ag)}^\circ$[3] (v)	$-\alpha_{H^+,s}^\circ$[12] (ev)	$-\alpha_{Ag^+,s}^\circ$ (ev)	$-\Delta\alpha_s^\circ$ (ev)		χ_s (v)
					(H)**	(Ag)**	
H_2O	0.40	−0.40	11.71	5.37	2.23	2.22	0.40
AN	0.19	−0.05*)	11.43	5.66	2.16	2.16	0.25
FA	0.54		11.81		2.20		0.37
MeOH	0.41		11.64		2.15		0.09
Py	0.63		11.27		1.56		
DMF		−0.10		5.57		2.12	
PC		−0.51		5.10		2.06	
NM		−0.47		5.04		1.96	
DMSO		0.05		5.39		1.79	

*): quoted from Ref. 11).

): the columns (H**) or (**Ag**) means the values calculated from $E_{s(H)}^\circ$ or $E_{s(Ag)}^\circ$.

AN-*acetonitrile*, **MeOH**-*methanol*, **FA**-*formamide*, **Py**-*pyridine*, **DMF**-*dimethylformamide*, **NM**-*nitromethane*, **PC**-*propylenecarbonate*, **DMSO**-*dimethylsulfoxide*.

couple for a series of solvents referred to the **Ag/0.01 N Ag$^+$** electrode in the same solvent. The standard electromotive force of the **Fer/Fer$^+$** couple referred to the standard **Ag/Ag$^+$** electrode may be obtained by subtracting 0.12 v from the values in the table[3], assuming that the activity coefficient of the **Ag$^+$** ion at 0.01 **N** concentration practically equals unity.

Table 2 shows the values of $-\Delta\alpha_s^\circ$ obtained in this way using the standard potentials of the **Fer/Fer$^+$** couple referred to the standard hydrogen or **Ag/Ag$^+$** electrode on the basis of Eq. (8 a) or (8 b).

Although there are a limited number of solvents in which the standard electromotive force of the **Fer/Fer$^+$** couple is measured against both of the reference electrodes of the hydrogen and silver electrodes, it can be seen from the comparison of the $-\Delta\alpha_o^s$-values in water and acetonitrile that there is no difference in the $-\Delta\alpha_s^\circ$-values whether they are obtained using $E_{s(H)}^\circ$ or $E_{s(Ag)}^\circ$. As seen from Table 2, there is little difference in the values of $-\Delta\alpha_s^\circ$ in water, acetonitrile, formamide and methanol, as expected from the molecular structures of ferrocene and ferricinium ion. Therefore the major part of the difference in $\varphi_{Fer/Fer^+,s}^\circ$ in these solvents may be attributed to the electrostatic part of solvation energy of ferricinium ion due to the surface potential of the solvent, since the difference may be given by Eq. (10),

$$\Delta\bar{\alpha}_s^\circ - \Delta\alpha_s^\circ = F\chi_s\,, \tag{9}$$

$$\delta\varphi_{Fer/Fer^+,s}^\circ = \delta(\Delta\alpha_s^\circ) + F\delta\chi_s\,, \tag{10}$$

where χ_s is the surface potential of solvent s. The values of χ_s are also listed in Table 2 for four solvents.

The value of $-\Delta\alpha_s^\circ$ estimated from $E_{s(H)}^\circ$ in pyridine and that estimated from $E_{s(Ag)}^\circ$ in dimethylsulfoxide are considerably lower than those in other solvents, indicating specific interactions of ferrocene and ferricinium ion with these solvent molecules.

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