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TECHNICAL REPORT

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An electrochemical reference system for use in different solvent media – The decamethylated ferricinium/ferrocene redox couple

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INTRODUCTION

The proposal of this technical report is justified by the difficulties met by electrochemists, electroanalysts, corrosionists, and biologists when electrode potentials measured in different non-aqueous or aqueous-organic solvents with reference to the familiar, commercially available, and very dependable, aqueous Saturated Calomel Electrode (SCE) are to be physically inter-compared on some “inter-solvental scale” of electrode potentials. These difficulties are caused by the occurrence of two basic extrathermodynamic factors, namely, the primary medium effect [1][1] on electrode potentials and the liquid-junction potentials between different solvent media. This report details the use of the half-wave potential of the ferricinium/ferrocene redox couple or the decamethyl derivatized ferricinium/ferrocene redox couple as the basis of a reference electrode system useful to compared measured electrode potentials to the aqueous saturated calomel electrode when used in various solvent systems.

For an acceptable approach to the solution of the above problem, superseding earlier attempts [2], Strehlow and co-workers [3], [4] proposed to use the redox couple ferricinium|ferrocene (in terms of its “half-wave potentials”, or “formal redox potentials”, obtainable from voltametric experiments in different solvents with the same supporting electrolyte and against the same working reference electrodes), for which, based on an extended experimental evidence, they assessed an “invariancy of potential” to within about ±15 mV in a dozen different solvents, assuming the above redox couple to be unaffected by solvent interactions. Principles and reasons for this choice were expounded in detail [3], [4] and need not be repeated here. Strehlow’s idea was later reassessed in nearly the same terms by Gritzner and Kůta [5], but various authors later demonstrated the existence of specific interactions of the ferricinium| ferrocene couple with some of the solvent media considered, thus partially impairing the intersolvental invariancy of the above redox potentials. However, recently [6], [7], [8], [9], and [10], it was shown that such residual solvent effects could be drastically abated by permethylation of the aromatic rings of the redox couple. For instance, the decamethyl-derivatized ferricinium|ferrocene couple, being chemically and electrochemically reversible, with half-wave potentials quite unaffected by the working solvent, lends itself as the best reference-potential redox couple known so far (besides other advantages with respect to the unmethylated parent couple, such as a more general chemical stability, and a more advantageous potential window compared to the operating reference electrode SCE is more advantageously placed). Therefore, what remains to be done by the user is to calibrate the aqueous SCE electrode (which, in common practice, is the reference electrode blindly and invariably used in contact with the non-aqueous solvents studied) versus the half-wave potential of the decamethylferricinium|decamethylferrocene [$Me_{10}Fec^+$|$Me_{10}Fec$] couple in the solvent studied, along the lines explained below, and to apply the consequent corrections to the measured potentials (see Table 1). The resulting corrected potentials will finally become intersolventally comparable.

An additional bonus to the present methodology is provided by the parallel decamethyl-derivatized cobalticinium|cobaltocene [$Me_{10}Coc^+$|$Me_{10}Coc$] redox couple because it also was shown to be chemically and electrochemically reversible and its half-wave potential E^* differs by a constant value from that of [$Me_{10}Fec^+$|$Me_{10}Fec$], in terms of E^*[$Me_{10}Coc^+$|$Me_{10}Coc$] = E^*[$Me_{10}Fec^+$|$Me_{10}Fec$] – 1,407 V, at 298,15 K.

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[1] Figures in square brackets refer to the Bibliography.

AN ELECTROCHEMICAL REFERENCE SYSTEM FOR USE IN DIFFERENT SOLVENT MEDIA – THE DECAMETHYLATED FERRICINIUM/FERROCENE REDOX COUPLE

1 Scope

The scope of this technical report is to present the background considerations which led to this compilation of potentials of the aqueous saturated calomel electrode compared to the cyclovoltametric data for a glassy carbon electrode in various solvent media. A tabulation of working potentials of this electrode pair in various solvent media is presented. A comparison of the cyclovoltametric scans for the ferricinium/ferrocene and deamethyl derivatized ferricinium/ferrocene redox couple system is presented and important features are discussed.

2 Tabulation of working potentials

Clause 2 gives an explanation of the basis for the tabulation of working potentials of the aqueous saturated calomel electrode compared to the ferricinium/ferrocene redox couple and the decamethyl derivatized ferricinium/ferrocene redox couple in various solvent media, as well as an identification of the voltametric range of these couples in various solvent media.

2.1 Working potentials of an SCE

Table 1 compiles the working potentials of the aqueous saturated calomel electrode compared to the ferricinium/ferrocene redox couple and the deamethyl derivatized ferricinium/ferrocne redox couple in various solvent media.

Table 1 – Working potentials of the aqueous SCE compared to the half-wave potential of the decamethyl derivatized ferricinium/ferrocene redox couple in various solvent media

Solvent	E_{SCE} / V[a]	References
Water	0,144	[7]
Methanol	0,124	[7]
Propylene carbonate	0,069	[7]
Methyl pyrrolidinone	–0,055	[8] to [10]
Acetone	0,021	[8] to [10]
Acetonitrile	0,119	[8] to [10]
Methylene chloride	0,060	[8] to [10]
Dimethyl formamide	0,008	[8] to [10]

[a] Values to be added to the potentials measured in the solvent studied versus the aqueous SCE to get them referred to the solvent-invariant half-wave potential of the $[Me_{10}Fec^{+}|Me_{10}Fec]$ redox couple.

NOTE Table 1 gives values for the aqueous SCE at 298K working potential (including insolvental liquid junction potentials) when compared to the decamethyl derivatized ferricinium/ferrocene redox couple

Ferrocene [Fec] is the dicyclopentadienyl ferrous complex; oxidation to the corresponding ferric complex (ferricinium, $[Fec^{+}]$) is a simple, chemically and electrochemically reversible one-electron process. The metal ion is buried at the centre of a nearly spherical, big complex; hence, these substances undergo negligible chemical or steric changes when oxidation or reduction occurs.

The half-wave potentials of [Fec$^+$|Fec] were first measured polarographically by Strehlow [3], [4] in concentrated aqueous sulfuric acid solutions with respect to the Hg_2SO_4 electrode in the cell (1):

$$\mathrm{Pt|[Fec^+|Fec]\ in\ aq.H_2SO_4 ¦ aq.H_2SO_4|Hg_2SO_4|Hg|Pt} \qquad (1)$$

combined with cell (2):

$$\mathrm{Pt|H_2\ (1\ bar)|aq.H_2SO_4|Hg_2SO_4|Hg|Pt} \qquad (2)$$

It is readily shown that

$$E_2 - E_1 = E°Hg_2SO_4 - E°H_2 - E^*Fec+|Fec + k\ pH \qquad (3)$$

Now, since in Equation (3) the constant term ($E°_{Hg2SO4} - E°_{H2} - E^*_{Fec+|Fec}$) is determinable, pH is here a true pH = $-\log(a_{H+})$ in superacid H_2SO_4 solutions, a quantity not attainable by the conventional IUPAC procedure, which is reliable only in the range $1 < pH < 13$, due to the increasing effect of residual liquid junction potentials at extreme pH. This interesting scheme can also be applied to other ultra-concentrated acid solutions (HCl, HBr, HI).

However, definitely, the most interesting and important opportunity is to use the Fec$^+$|Fec couple in its improved decamethylated form [6], [7], [8], [9], and [10], Me$_{10}$Fec$^+$|Me$_{10}$Fec, as one tool of invariant potential across different solvents, i.e. entering into an “intersolvental” scale of electrode potentials. In this context, to attain the solvent-invariant potential of the [Me$_{10}$Fec$^+$|Me$_{10}$Fec] redox couple, the pertinent half-wave potential or formal redox potential can be obtained in voltametric experiments on a stationary, solid working electrode (such as glassy carbon or platinum, which can be reproducibly polished according to a severe protocol) compared to the same operating aqueous SCE reference electrode in the same supporting electrolyte, and with careful compensation of the residual ohmic drops. The half-wave potential values sought can be obtained, either

a) as the average of the anodic and cathodic peak potentials in cyclic voltametry experiments (typically resulting in symmetric peak signals); or

b) from the waves obtained in “stationary” experiments (i.e., performed at very low scan rates, as in the case of polarography) or, more realistically, from the convolutive analysis of the above-mentioned peak signals [6], [7], [8], [9], and [10].

Accumulation of data for completion of Table 1 is under way.

2.2 Cyclovoltametric characteristics

The cyclovoltametric behaviour of the ferricinium/ferrocene and decamethyl derivatized ferricinium/ferrocene redox couples in various solvent media is shown in Figure 1.

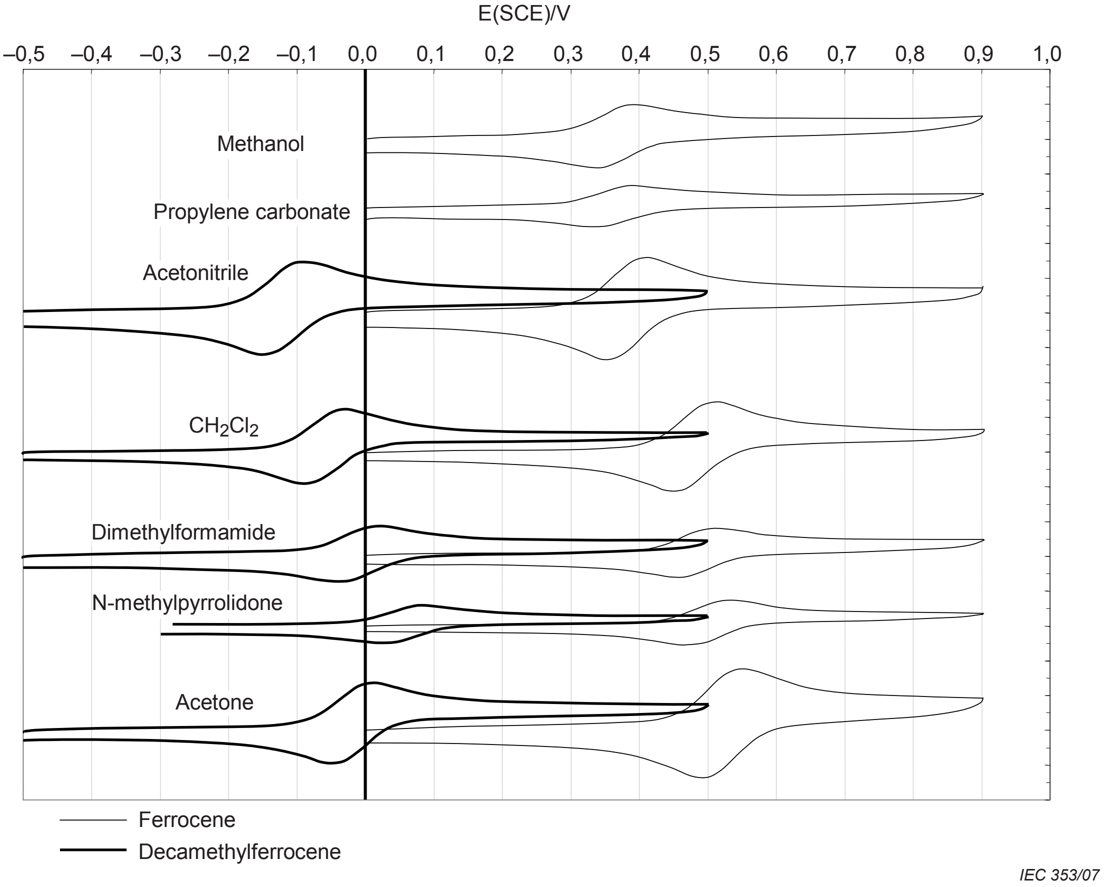

Figure 1 – Synopsis of cyclovoltametric characteristics obtained for redox couples $Fec^+|Fec$ (thin curves) and $Me_{10}Fec^+|Me_{10}Fec$ (thick curves) at 298 K, and 0,2 V s^{-1} scan rate, on a glassy carbon electrode, versus the operational reference aqueous SCE electrode, in different solvents with constant 0,1 M TBAP (tetra butyl ammonium perchlorate) supporting electrolyte

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