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

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

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

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IEC 62456 which is a technical report, has been prepared by subcommittee 65D: Analysing equipment, of IEC technical committee 65: Industrial-process measurement and control.

The text of this technical report is based on the following documents:

Enquiry draft	Report on voting
65D/125/DTR	65D/127/RVC

Full information on the voting for the approval of this technical report can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

The committee has decided that the contents of this publication will remain unchanged until the maintenance result date indicated on the IEC web site under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

A bilingual version of this publication may be issued at a later date.

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.

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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.