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**RECOMMENDATIONS ON REPORTING
ELECTRODE POTENTIALS IN
NONAQUEOUS SOLVENTS**

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Abstract - This report recommends that the redox couples ferrocene/
ferricenium ion [ferrocene: bis(η -cyclopentadienyl)iron(II)] and
bis(biphenyl)chromium(I)/bis(biphenyl)chromium(0) be employed as
reference redox systems. Procedures for measuring and reporting electrode
potentials in nonaqueous solvents versus these reference redox systems
are presented. The difference in electrode potentials for ferrocene/
ferricenium ion and bis(biphenyl)chromium(0)/bis(biphenyl)chromium(I) ion
for 22 solvents obtained by polarography and cyclic voltammetry are
listed. Both of the recommended redox systems approach a solvent
independent redox system as closely as presently known. Electrode
potential data reported versus these systems permit the comparison of
electrode potentials for a given system in different nonaqueous solvents
and thus allow studies of solvent effects on electrode potentials in
nonaqueous systems by compiling and comparing data obtained in different
solvents.

INTRODUCTION

Electrochemical research activities in nonaqueous solvents have steadily increased over the past thirty years. A considerable number of these studies employed polarographic, voltammetric and to a lesser degree potentiometric techniques to learn about the redox behaviour of inorganic and organic compounds in nonaqueous solvents. The interests of different research groups varied. Some used nonaqueous solvents only because the compounds of interest were not soluble in water, some were seeking new analytical techniques, some were primarily interested in electrode kinetics, others only in the products obtainable by an electrochemical process in nonaqueous solvents. Thus in reporting the experimental data emphasis was generally placed on those parameters that were of particular interest to the researcher. In many of these studies very little attention has been given to the reference electrode used. Quite frequently electrode potentials have been reported versus aqueous reference electrodes such as the calomel electrode, the silver-silver chloride electrode or the standard hydrogen electrode in water. Many of the experimental arrangements that have been employed included liquid junction potentials. Although some experimental arrangements had phase boundaries that yielded stable liquid junction potentials and some research groups reported reproducible values for the liquid junction potentials, very often the tacitly made assumption of a stable and reproducible liquid junction potential was not justified. Even some of the reference electrodes proposed in the nonaqueous solvents studied did not yield stable and reproducible potentials, thus many of the data obtained versus reference electrodes in the same medium have also to be viewed with caution. Many of the electrode potentials reported in literature have been measured under conditions that are not reproducible and therefore of little or no value. Furthermore potential differences of reliable reference electrodes in nonaqueous solvents have rarely been measured, preventing comparisons between electrode potentials in a given solvent as reported by different research groups. For these reasons, compilation of definite and reliable electrode potentials in nonaqueous solvents has been severely hindered. It is therefore necessary to agree on some procedures to measure and report electrode potentials versus generally accepted standards. There are several possibilities for such standards available at this time.

One would be to agree upon one reference electrode for each solvent and measure redox potentials versus this reference electrode under conditions that are free of any liquid junction potential. It would also be conceivable that one redox system could serve in the respective solvents as a reference electrode. The system silver, silver perchlorate or silver nitrate, dissolved in the nonaqueous solvent under study has been used (ref. 1). The drawback of such reference electrodes is that while yielding stable potentials in several solvents, decomposition limits the application in others.

Another possibility is the use of reference redox systems. The concept of a reference redox system has been developed during studies to find redox systems the electrode potentials of which are only modestly affected by the nature of the solvent. Preferably such variation in the electrode potentials should be smaller than the experimental error.

EXAMPLES OF REFERENCE REDOX SYSTEMS PROPOSED IN LITERATURE

Pleskov (ref.2) was the first to suggest such an idea and proposed the redox systems Rb^+/Rb and $\text{Rb}^+/\text{Rb}(\text{Hg})$ respectively as such a reference redox system assuming that, because of the large ionic radius of Rb^+ , changes in the Gibbs energy of solvation of this ion would be small. It was later found that the changes in the Gibbs energy of solvation of Rb^+ are too large to be ignored (ref.3).

A very thorough study by Strehlow and coworkers on various organometallic complexes has led to the formulation of the following requirements for a suitable reference redox system (ref.3): (i). The ions or molecules forming the reference redox system should preferably be spherical with as large a radius as possible, (ii) the ions should carry a low charge, (iii) the equilibrium at the electrode should be rapid and reversible, (iv) both components of the redox couple should be soluble, (v) no change in the geometry of the ligands should occur, (vi) the redox potential should be in a potential range that is accessible in as many solvents as possible and (vii) both forms should be stable enough to permit potentiometric measurements. Strehlow suggested the systems ferrocene/ferricenium ion (ferrocene is bis-(η -cyclopentadienyl)iron(II)) and cobaltocene/cobalticenium ion (cobaltocene is bis-(η -cyclopentadienyl)cobalt(II)). Besides these two several other reference redox systems have been suggested and used, such as tris(2,2'-bipyridine)iron(I)/tris(2,2'-bipyridine)-iron(0) (ref.4), bis(biphenyl)chromium(0)/bis(biphenyl)chromium(I) ion (ref.5,6) and redox systems based on polynuclear aromatic hydrocarbons and the respective radical ions (ref.7).

It is not the purpose of this recommendation to discuss the various extrathermodynamic assumptions to obtain single ion properties in nonaqueous solvents, this has been done already in various articles (ref.8-10). The possibility to calculate such data would only be an additional benefit in reporting electrode potential versus such systems. The prime object must be to agree on a procedure to obtain reliable values for electrode potentials in nonaqueous solvents.

RECOMMENDED REFERENCE REDOX SYSTEMS

For pragmatic reasons, namely the ease with which such reference redox systems can be used experimentally, especially in polarography and voltammetry - the two most commonly employed techniques - and the added benefit to use data already reported versus such reference redox systems, it is recommended that electrode potentials in nonaqueous solvents be reported versus a reference redox system.

As mentioned earlier the number of proposed reference redox systems has increased over the years. While each reference redox system may have its merits as an extrathermodynamic assumption, it is necessary to limit ourselves to two such reference redox systems. A greater number would defeat the purpose of this recommendation and would again hinder an easy compilation of electrode potentials in nonaqueous solvents. Although one reference redox system should be the ultimate goal, two are suggested for the present, since not every reference redox system can be used in all solvents. In order to maintain the same experimental conditions the reference redox system is added to the solution studied with exclusion of air and water. Quite often the redox potential of a reference redox system will coincide with the redox potential of the species under study, making the evaluation of data obtained by polarographic and voltammetric techniques difficult. These problems can be circumvented by use of two reference redox systems, the potential differences of which have been determined.

Any selection of two out of several published reference redox systems must be somewhat arbitrary. It is recommended that the two systems ferrocene/ferricenium ion and bis(biphenyl)chromium(0)/bis(biphenyl)chromium(I) ion be used as reference redox systems. Both systems fulfill the requirements for reference redox systems in many solvents. The difference between the respective redox potentials of these two reference systems has been found to be almost constant in a variety of solvents (cf. refs. 11, 15-17; Table 1). The observed deviation from the average value of 1.124 V obtained for 22 solvents was ± 12 mV, which is somewhat larger than the experimental error of ± 4 mV.

For polarographic and voltammetric measurements where only one form of the redox system has to be added to the solution, ferrocene and bis(biphenyl)chromium tetraphenylborate* should be used.

* Note: Small amounts of bis(biphenyl)chromium tetraphenylborate can be obtained upon request from G. Gritzner, Institut für Chemische Technologie Anorganischer Stoffe, Johannes-Kepler-Universität Linz, A-4040 Linz / Auhof, Austria

This recommendation, however, should not discourage further studies on reliable reference electrodes in nonaqueous solvents nor should it discontinue the search for a more nearly "ideal" reference redox system to report standard electrode potentials on a solvent independent scale. It is merely asked that electrode potentials versus one of the two recommended reference redox systems, measured under conditions outlined in this paper, should be included among the experimental data and that the redox behaviour of these two systems should also be investigated for solvents in which such work has not yet been carried out. Besides facilitating the compilation of electrode potentials in nonaqueous solvents the use of a reference redox system in reporting electrode potentials would be of considerable assistance in obtaining further information on the possibility of establishing a scale of standard electrode potentials in nonaqueous solvents and in increasing our understanding of the solvent effects on the behaviour of redoxactive species.

Note: A distinction is made in this recommendation between the expressions "reference electrode" and "reference redox system". The expression reference electrode is used for an electrode with a known, invariant, electrode potential as defined under 8.9 in the Manual of Symbols and Terminology for Physicochemical Quantities and Units, Appendix III - Electrochemical Nomenclature (PAC 37 (1974) 501). The expression reference redox system is reserved for the recommended systems: ferrocene/ferricenium ion and bis(biphenyl)-chromium(0)/bis(biphenyl)chromium(I) ion.

The reference redox systems can be used in arrangements typical for a reference electrode e.g. a platinum wire in contact with an equimolar mixture of ferrocene and ferricenium picrate in the solvent under investigation. Such a setup will be preferred in potentiometric measurements. In polarographic and voltammetric studies however it is sufficient to add one form of the reference redox system (ferrocene or bis(biphenyl)chromium(I) tetraphenylborate) to the solution under study. The other form of the redox couple is formed at the working electrode during the measurement while a current is passed. In case of fast electrode kinetics the redox potential measured will agree to the conditional standard potential for this system. Quite frequently such measurements will be carried out in a three electrode arrangement with reference electrodes other than the recommended reference redox system serving as a reference electrode.

The expression "pilot ion" has been used in the past to specify the technique of adding only one form of the redox couple. The expression pilot ion however does not seem to be fully adequate since in any case it is a redox system which is used as a reference system not one form of the redox couple only.

RECOMMENDATIONS FOR MEASURING ELECTRODE POTENTIALS IN NONAQUEOUS SOLVENTS

It is of prime importance that all measurements by polarographic and voltammetric techniques are made versus reference electrodes the potentials of which do not change during the time of the experiment. If liquid junctions are part of the experimental arrangement it is mandatory that the liquid junction potential remains constant within the experimental error during the time of measurement. The stability of the reference electrode and the liquid junction potential (if included) should be checked carefully. If no variation has been observed in the obtained potential values for the redox system under investigation, a solution containing the same concentration of the supporting electrolyte and the reference redox system should be added to the solution under study with strict exclusion of air and water. After this addition both the studied redox system and the reference redox system should be measured at least twice versus the reference electrode. The potential data of the studied redox system before and after the addition of the reference redox system measured versus the reference electrode should agree within the limits of experimental error. The difference in potentials between the studied redox system and the reference redox system can then be calculated. The data for the two measurements must agree within the experimental error.

If a stable reference electrode without liquid junction is used in polarographic and voltammetric measurements it is sufficient to measure the redox potential of ferrocene and bis(biphenyl)chromium(I) tetraphenylborate versus such an electrode. For solvents in which these reference redox systems have not been studied, the polarographic and voltammetric behaviour of these systems should also be investigated.

Potentiometric measurements versus the suggested reference redox systems as a reference electrode should be done in arrangements without a liquid junction. Care should be taken that such electrodes yield stable and reproducible data. Since a slow decomposition of the ferricenium ion or the bis(biphenyl)chromium compounds may occur in several solvents, freshly prepared electrodes should be used. As in any studies in nonaqueous media the purity of the solvent under investigation is of utmost importance. Great care should be taken in purifying the solvents; the methods of purification should either be reported or reference given to published procedures. Since traces of water or other impurities may still be present

TABLE 1 Difference between $E_{1/2}$ or $1/2(E_{pa}+E_{pc})$ values, * for ferrocene and bis(biphenyl)chromium tetrphenylborate (ΔE) in tetraethylammonium perchlorate solutions (conc: 0.1 mol l⁻¹) and/or tetrabutylammonium perchlorate solutions (conc: 0.1 mol l⁻¹) in 22 solvents^(a). ($T = 298$ K)

Solvent	Reference no:	ΔE (Ferrocene-bis(biphenyl)-chromium(I))
1,2-Dichloroethane	(11)	1.13 ₁ ^(b)
Dichloromethane	(11) ^(d)	1.14 ₈ ^(b) 1.15 ₂ ^(c)
Nitromethane	(11)	1.11 ₂
Nitrobenzene	(11)	1.13 ₀
Acetonitrile	(11)	1.11 ₈ ^(b) 1.11 ₉
Propylene carbonate	(11)	1.11 ₄
Butyrolactone	(11)	1.11 ₂
Acetone	(11)	1.13 ₀
Methanol	(11)	1.13 ₄
Ethanol	(11)	1.13 ₄
<u>N,N</u> -Dimethylformamide	(11)	1.12 ₇
Methyl-2-pyrrolidinone	(11)	1.12 ₆
Dimethyl sulfoxide	(11)	1.12 ₃
Tetramethylene sulfone	(11)	1.11 ₄ ^(b)
<u>N,N</u> -Dimethylacetamide	(16)	1.13 ₁
<u>N,N</u> -Diethylacetamide	(16)	1.13 ₅ ^(b)
Formamide	(16)	1.12 ₉ ^(b)
Trimethyl phosphate	(16)	1.13 ₀ ^(b)
Tetramethylurea	(16)	1.13 ₀ ^(b)
Hexamethylphosphoric triamide	(16)	1.12 ₄
<u>N</u> -Methylformamide	(17)	1.13 ₅ ^(b)
2,2'-Thiodiethanol	(15)	1.12 ₁ ^(b)

(a) For further data such as ($E_{3/4}-E_{1/4}$), ($E_{pa}-E_{pc}$), etc. see references 11, 15-17

(b) Tetrabutylammonium perchlorate solution (conc: 0.1 mol l⁻¹)

(c) Saturated solution of tetraethylammonium perchlorate

(d) Ferrocene undergoes an irreversible electrode reaction in dichloromethane

* Bis(biphenyl)chromium(I) tetrphenylborate can be studied polarographically on the dropping mercury electrode and by cyclic voltammetry on the stationary platinum electrode. The $E_{1/2}$ and $1/2(E_{pa}+E_{pc})$ values were found to agree within ± 1 mV. The same holds true for ferrocene in those cases where ferrocene can be studied on the dropping mercury electrode.

even upon careful purification of the solvent, the concentration of such impurities should be reported; they may or may not affect the redox behaviour of the investigated species. Their controlled addition to the solution under study will yield such information and should be carried out.

RECOMMENDATION ON REPORTING ELECTRODE POTENTIALS IN NONAQUEOUS SOLVENTS VERSUS A REFERENCE REDOX SYSTEM

It is recommended that electrode potentials of systems under study be reported directly with respect to whichever of the two reference redox systems is chosen, in all solvents and at all temperatures (insofar as possible). Potentiometric measurements should be made in cells without liquid junctions. Salt bridges should be avoided if possible. In any case a detailed description of the apparatus should be given.

Electrode potentials measured by polarographic and voltammetric techniques are generally made in solutions containing a supporting electrolyte. While it is usually assumed (and in many cases true) that tetraalkylammonium perchlorates, most commonly employed as supporting electrolytes, do not significantly affect redox potentials, cases have been reported where altering the cation (ref.12) or the anion (ref.13) of the supporting electrolyte significantly changed the redox potentials of redox active species. During studies of organic compounds leading to radical cations or anions and of the redox behaviour of metal complexes it was noticed that even small amounts of metal cations or anions significantly affected half wave and peak potentials (ref.14). It is therefore mandatory that the nature and the concentration of the supporting electrolyte and of any other compound in solution besides the redox system of interest are reported in the publication.

All data should be reported as "crude" data first, omitting any corrections for ion-pair formation or activity coefficients. While such correction can be made in the further evaluation of the data, the absence of the crude data may prohibit the evaluation as improved models for ion-pair formation or activity coefficients become available.

Abbreviations: It is recommended that the abbreviation Fc be used for the reference redox system ferrocene/ferricenium ion and BCr for bis(biphenyl)chromium(0)/bis(biphenyl)-chromium(I) ion. These abbreviations should be added when symbols for redox potentials are given in the text or in figures, for example $E_{1/2}(\text{BCr})$ or E_{Fc}° . When specifying the respective reference redox systems, the following abbreviations are suggested: Fc/Fc⁺ and BCr/BCr⁺. Such abbreviations however should only be used in a publication after specifically defining the names of the compounds to which they refer.

GIBBS ENERGIES OF TRANSFER

Both reference redox systems have also been employed as extrathermodynamic assumptions to calculate Gibbs energies of transfer of single ions. Such data have generally been obtained from polarographic half wave potentials of cations that are reversibly reduced to metal amalgams. It is recommended that the extrathermodynamic assumption employed be indicated by abbreviations such as $\Delta G_{\text{tr}}^{\circ}(\text{Fc})$ when reporting Gibbs energies of transfer. Again the meaning of such abbreviations must be defined in each publication.

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