Chapter 2
# Reference Redox Systems in Nonaqueous Systems and the Relation of Electrode Potentials in Nonaqueous and Mixed Solvents to Standard Potentials in Water

Gerhard Gritzner

2.1 Introduction

NOTE: Throughout this chapter recommendations by the International Union of Pure and Applied Chemistry (IUPAC) [1, 2] for representing electrochemical cells will be followed stating that a single vertical bar (|) should be used to represent a phase boundary, a dashed vertical bar (¦) to represent a junction between miscible liquids, and a double dashed bar (¦¦) to represent a liquid junction, in which the liquid junction (potential) is assumed to be eliminated. The subscripts account for the following: (s), solid; (l), liquid; (aq), aqueous; and (Hg), amalgam. A slash (/) is used for cases where both forms of the redox couple are assumed to be in solution.

   As electrochemistry moved into mixed and nonaqueous electrolytes it became of interest to compare potentials in different media. Serious problems preventing comparison are the liquid junction potentials between different electrolytes. Such liquid junction potentials also occur in the measurement in aqueous systems, but they are generally suppressed by a salt bridge. Salt bridges for aqueous systems usually consist of (saturated) solutions of KCl or NH_4NO_3. For both KCl and NH_4NO_3 similar mobilities for the cation and the anion of the respective salt were measured in aqueous solutions. Thus the liquid junction potential between two aqueous electrolytes connected via such a bridge should be smaller than the experimental error (see Chap. 1). Data in aqueous systems without liquid junction potentials are obtained from measurements in cells without transference such as:

$$Pt|H_2(g, p = p°)|HCl(aq, a_± = 1)¦HCl(aq, a_± = 1)|AgCl|Ag.$$
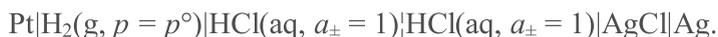
   A liquid junction potential will, however, occur even in water whenever the activity of HCl $[a_±(HCl)]$ on the right differs from the activity of HCl on the left.

G. Gritzner (✉)
Institut für Chemische Technologie Anorganischer Stoffe, Johannes Kepler Universität, Altenbergerstraße 69, 4040 Linz, Austria
e-mail: Gerhard.Gritzner@jku.at

An electrochemical cell consisting of an aqueous and a nonaqueous half-cell or two different nonaqueous solvents in the half-cells always includes a liquid junction potential. Quite frequently the liquid junction potential is ignored and aqueous reference electrodes such as the silver–silver chloride electrodes in various concentrations of KCl or calomel electrodes are used. Care was at best taken that water cannot diffuse into the nonaqueous system. It is important to note that the liquid junction potential is a transport—not a thermodynamic—property (see Chap. 3). This is generally ignored or not fully understood. Thus the literature is full of papers for conversion factors to aqueous reference electrodes [3]. Experimental evaluations of liquid junction potentials were carried out, but always refer to a given setup of the junction [4]. Its value depends on the design of the diaphragm and on time. Thus a given reference cell with a special diaphragm may yield reproducible data when used in electrochemical measurements. However, the reported potential includes the unknown liquid junction potential. Thus using the very same reference electrode may—due to a different separator—yield different potential values. Electrochemical measurements in the same electrolyte, on the other hand, always present thermodynamic values and thus reproducible values (within the experimental skills of the researcher).

Two different approaches are used to establish electrochemical series in nonaqueous and mixed aqueous–nonaqueous systems: (1) a reference redox system [5] or (2) a reference electrode in combination with a bridge to suppress the liquid junction potential [6].

2.2   Reference Redox Systems

Pleskov proposed the redox systems $Rb^+|Rb$ and $Rb^+|Rb(Hg)$, respectively, as reference redox systems (pilot ion) to correlate data in aqueous and nonaqueous systems [7]. He proposed this system, because of the large ionic radius of Rb^+, assuming that interactions of solvent molecules with the Rb^+ cation would be small. His assumption was strongly influenced by the Born model [8]. The Born model is based on purely electrostatic considerations and considers the change in Gibbs energy of an ion by the transfer from vacuum into water. The dominating properties in such transfer are the ionic charge and the ionic radius. The larger the radius and the smaller the charge, the weaker is the ion solvent–ion interaction according to the Born model. Such consideration made Pleskov to propose the redox systems $Rb^+|Rb$ and $Rb^+|Rb(Hg)$ as reference (pilot ion).

Studies on Gibbs energies of transfer of Rb^+ [9–11] showed that the interaction of Rb^+ with different solvents is not negligible. The $Rb^+|Rb$ couple turned out to be too much solvent dependent to be used as a reference redox system to relate electrochemical properties in different solvents.

Strehlow and coworkers studied various organometallic complexes. They formulated requirements for suitable reference redox systems [12] (1) The ions or molecules forming the reference redox system should preferably be spherical with as

large a radius as possible, (2) the ions should carry a low charge, (3) the equilibrium at the electrode should be rapid and reversible, (4) both components of the redox couple should be soluble, (5) no change in the geometry of the ligands should occur upon the redox process, (6) the redox potential should be in a potential range that is accessible in as many solvents as possible, and (7) both forms should be stable enough to permit potentiometric measurements. Strehlow suggested the systems ferrocene/ferrocenium ion (ferrocene: *bis*(η-cyclopentadienyl)iron(II)) and cobaltocene/cobaltocenium ion (cobaltocene: *bis*(η-cyclopentadienyl)cobalt(II)). While some of the arguments used in this publication are strongly influenced by the Born concept of ion–solvent interactions, this paper became very influential in establishing reference redox systems. Unfortunately the ferrocenium/ferrocene couple is affected by interactions of water with the ferrocenium ion. Thus the ferrocenium/ferrocene couple should not be used in water, making this couple unsuited for establishing a general electrochemical series versus the standard hydrogen electrode [13]. The ferrocenium ion/ferrocene couple consists of cation and a neutral molecule. It is the typical example of a cation/neutral analogue redox couple. Studies in ionic liquids indicate problems with the ferrocenium ion/ferrocene couple [14]. Cobaltocenium ion/cobaltocene, which was also used in nonaqueous solvents but never properly connected to the ferroceniumion ion/ferrocene scale [15, 16], is currently favored in electrolytes based on ionic liquids, but recent publications indicate that ferrocenium ion/ferrocene and *bis*(biphenyl)chromium(I)/*bis*(biphenyl)chromium(0) may also be used in room temperature ionic liquids [17, 18]. Decamethylferrocene was later suggested to be superior to ferrocene due to its larger ionic radius [19, 20] as claimed by the authors.

Other reference redox systems have been proposed and used, such as *tris*(2,2′-bipyridine)iron(I)/*tris*(2,2′-bipyridine)iron(0) [21], 4,7-dimethyl-1,10 phenanthroline iron(II) [4], and redox systems based on polynuclear aromatic hydrocarbons and the respective radical ions [22–24].

Most data in nonaqueous and mixed solvents have been published versus the *bis*(biphenyl)chromium(I)|*bis*(biphenyl)chromium(0) redox couple [25].

The use of reference redox systems became very popular in connection with polarographic and cyclovoltammetric studies. Generally the respective reference redox system was added to the electrolyte with the studied redox system, thus avoiding any liquid junction potential (internal standard). An additional advantage of using a reference redox system is that only one form of the redox couple may be used. The second partner of the redox couple is generated during the polarographic or cyclovoltammetric study. In the case of the redox couple the oxidized form *bis*(biphenyl) chromium(I) tetraphenylborate [25] (earlier *bis*(biphenyl)chromium(I) iodide [26] is added; in case of the ferrocenium ion/ferrocene couple the reduced form, namely, ferrocene, is added.

2.3   Reference Electrodes in Combination with a Bridge

Pleskov, during his investigations in acetonitrile, introduced the system Ag|
0.1 mol dm^{-3} AgNO$_3$ as a reference electrode in this solvent [27]. This electrode,
later coined Pleskov electrode [28], is an electrode of the first kind. Reversibility of
the Ag$^+$|Ag system in many nonaqueous electrolytes led to reference electrodes based
on Ag$^+$|Ag in many solvents. Reversibility of this electrode was proven in some
solvents by varying the Ag$^+$ concentration and observing Nernstian behavior of the
electrode in a Ag$^+$ salt solution, maintaining constant ionic strength by adding a
supporting electrolyte. Measurements of such a reference electrode with the same
supporting electrolyte in both half-cells should yield potentials free of liquid junction
potentials. Thus one could establish an electrochemical series in the solvent chosen.
But such series are solvent specific and do not allow comparison of potential data in
different solvents. Thus an assumption is necessary to allow establishing a universal
scale of redox potentials.

Such an assumption was proposed, namely that a bridge consisting of a
0.1 mol dm^{-3} tetraethylammonium picrate in acetonitrile suppresses the liquid
junction potential between two different nonaqueous electrolytes [6]. The argument
in favor of such a salt bridge for nonaqueous electrolytes is the similar electrical
mobility of the tetraethylammonium cation and the picrate anion in acetonitrile. This
assumption was later expanded to allow for other nonaqueous solvents [28]. Agree-
ment for the electrochemical data was found if the nonaqueous solvents did not have
acidic hydrogen atom(s) in the solvent molecule (aprotic solvents) [29]. 0.1 mol dm^{-3}
solutions of either tetrabutylammonium picrate or pyridinium trifluorosulfonate [30]
were also used.

Occasionally also the use of so-called pseudo "reference electrodes" has been
reported (see Chap. 14). Such "pseudo reference electrodes" became popular in
polarography but especially in cyclic voltammetry, employing three electrode
arrangements. They consist of a silver or platinum wire or activated carbon dipping
into the electrolyte. They substitute for a reference electrode. Such electrodes were
reported to exhibit very stable potentials. The ease of such an arrangement was also
used in electrochemical studies in (room temperature) ionic liquids. It must be
pointed out that electrode potentials versus such electrodes are meaningless as such
arrangements do not constitute thermodynamic values.

2.4   Concentration and Activities

Electrochemical measurements especially in polarography and cyclic voltammetry
are frequently carried out in the presence of a supporting electrolyte. Concentrations
of the supporting electrolyte in aqueous and nonaqueous solutions are usually
0.1 mol dm^{-3}, but may reach 1 mol dm^{-3} or more. Analysis of activity coefficients
for the salt under study is not possible. Conductance studies in nonaqueous solvents

were carried out and equations to analyze 1:1 and later 2:2 and other symmetrical and unsymmetrical electrolytes were developed. From such measurements association constants were derived.

2.5   Summary and Recommendation

Electrode potentials should only be reported in thermodynamic arrangements. The most convenient way in polarography and cyclic voltammetry is the use of a reference redox system in the same electrolyte as the system under study. The $Ag^+|Ag$ electrode seems applicable to many solvents and may be used as reference electrode in potentiometric investigations.

There are two aspects to reference redox systems. One point is the possibility of compiling electrode potentials in a variety of solvents and solvent mixtures, which are not affected by unknown liquid junction potentials. Unfortunately very frequently aqueous reference electrodes are employed in electrochemical studies in nonaqueous electrolytes. Such data, however, include an unknown, irreproducible phase boundary potential. Electrode potentials of a redox couple measured in the same electrolyte together with the reference redox system constitute reproducible, thermodynamic data. In order to stop the proliferation of—in the view of the respective authors— better and better reference redox systems, the IUPAC recommended that either ferrocenium ion/ferrocene or *bis*(biphenyl)chromium(I)/*bis*(biphenyl)chromium(0) be used as a reference redox system [5].

The second point is the assumption that the potential of a half-cell containing the reference redox system is—within experimental error—independent of the nature of the solvent. This assumption is outside the realm of exact thermodynamics and thus open to discussion. As for any extra-thermodynamic assumption it is impossible to prove its validity. This point should be kept in mind especially when discussing single-ion transfer properties.

2.6   The Relation of Redox Potentials in Nonaqueous or Mixed Electrolytes to the Aqueous Standard Hydrogen Electrode

The conversion to the aqueous standard hydrogen electrode as reference half-cell requires an extra-thermodynamic assumption, either the assumption of a solvent independent reference redox system or other assumptions employed in calculating single-ion transfer properties. Details about the procedure and data for univalent cation|metal systems were published [13]. The redox couple ferrocenium ion/ferrocene as reference electrode system is not very suited for such a conversion as the ferrocenium cation undergoes interactions with water and thus impairs the extra-thermodynamic assumption for aqueous solutions. This becomes apparent when

Table 2.1 Difference of the half-wave potentials and ½ (E_{pa} + E_{pc}) potentials, respectively, of the ferrocenium ion/ferrocene and *bis*(biphenyl)chromium(I)/*bis*(biphenyl)chromium couples in several solvents

Solvent	Abbr.	$\Delta E_{(Fc-BCr)}$[a]	Solvent	Abbr.	$\Delta E_{(Fc-BCr)}$[a]
1,2-Dichlorethane	DCE	1.131	*N*-Methylformamide	NMF	1.135
Nitromethane	NM	1.112	*N,N*-Dimethylformamide	DMF	1.127
Nitrobenzene	NB	1.130	*N,N*-Dimethylacetamide	DMA	1.131
Acetonitrile	AN	1.118	*N,N*-Diethylacetamide	DEA	1.135
Propylene carbonate	PC	1.114	*N*-Methylpyrrolidone(2)	NMP	1.126
Butyrolactone	BL	1.112	Tetramethylurea	TMU	1.130
Acetone	AC	1.130	Dimethylsulfoxide	DMSO	1.123
Methanol	MeOH	1.134	Tetramethylene sulfone	TMS	1.114
Ethanol	EtOH	1.134	2,2′-Thiodiethanol	TDE	1.121
Formamide	FA	1.129	Trimethyl phosphate	TMP	1.130
Water	W	0.98	Hexamethylphosphoric triamide	HMP	1.124

[a]Difference in the electrode potentials of ferrocenium/ferrocene and *bis*(biphenyl)chromium(I)/ *bis*(biphenyl)chromium(0)

comparing the difference in electrode potentials for the ferrocenium ion/ferrocene couple and the *bis*(biphenyl)chromium(I)/*bis*(biphenyl)chromium(0) redox couples (Table 2.1). Most of the organic reference redox couples (at least one form) are practically insoluble in water. This makes measurement of reliable electrode potentials very difficult. In some solvents the electrode potential of the ferrocenium ion/ferrocene couple is more positive than the solvent oxidation (especially in sulfur donor solvents) and thus cannot be measured.

Table 2.1 clearly shows that the water value for the relation between ferrocene and bis(biphenyl)chromium ($\Delta E_{(Fc-BCr)}$) is too small and transfer properties using ferrocene as base from water will be incorrect.

References[1]

1. Quack M, Stohner J, Strauss HL, Takami M, Thor AJ, Cohen ER, Cvitas T, Frey JG, Holström B, Kuchitsu K, Marquard R, Mills I, Pavese F (eds) (2007) Quantities, units and symbols in physical chemistry, 3rd edn. RSC Publishing, Cambridge
2. Mills I, Cvitas T, Homann K, Kallay N, Kuchitsu K (1991) Quantities, units and symbols in physical chemistry, 2nd edn. Blackwell Science, Oxford. ISBN 0-632-03583-8
3. Pavlishuk VV, Addison AW (2000) Inorg Chim Acta 298:97
4. Nelson IV, Iwamoto RT (1961) Anal Chem 33:1795
5. Gritzner G, Kůta J (1983) Pure Appl Chem 56:461
6. Owensby DA, Parker AJ, Diggle JW (1974) J Am Chem Soc 96:2683

---

[1] The author apologizes for not including all pertinent references, but such references are cited in the respective publication and may be checked there.

7. Pleskov VA (1947) Usp Chim 16:2514
8. Born M (1920) Z Phys 1:45
9. Gritzner G, Auinger M (2009) Acta Chim Slov 56:86
10. Cox BG, Hedwig GR, Parker AJ, Watts DW (1974) Aust J Chem 27:477
11. Johnsson M, Persson I (1987) Inorg Chim Acta 127:15
12. Koepp HM, Wendt H, Strehlow H (1960) Z Elektrochem 64:483
13. Gritzner G (2010) J Mol Liq 156:103
14. Sukardi SK, Zhang J, Burgar I, Horne MD, Hollenkamp AF, MacFarlane DR, Bond AM (2008) Electrochem Commun 8:250
15. Behr B, Gutknecht J, Schneider H, Stroka J (1978) J Electroanal Chem 86:289
16. Topolev VV, Khanova LA, Krishtalik LI (2006) Chem Phys 326:33
17. Waligora L, Lewandowski A, Gritzner G (2009) Electrochim Acta 54:1419
18. De Vreese P, Haerens K, Matthijs E, Binnemans K (2012) Electrochim Acta 76:242
19. Bashkin JK, Kinlen PJ (1990) Inorg Chem 29:4507
20. Noviandri I, Brown KN, Fleming DS, Gulyas PT, Lay PA, Masters AF, Phillips L (1999) J Phys Chem B 103:6713
21. Tanaka N, Ogata T (1974) Inorg Nucl Chem Lett 10:511
22. Madec C, Courtez-Coupez J (1977) J Electroanal Chem 84:177
23. Bauer D, Beck J-P (1973) Bull Soc Chim (France) 1252
24. Kakutani T, Morihori Y, Senda M, Takahashi R, Matsumoto K (1978) Bull Chem Soc Jpn 51:2847
25. Gritzner G (1990) Pure Appl Chem 62:1839
26. Duschek O, Gutmann V (1973) Monatsh Chem 104:990
27. Pleskov VA (1948) J Phys Chem USSR 22:351
28. Diggle JW, Parker AJ (1973) Electrochim Acta 18:975
29. Gritzner G (2010) J Chem Eng Data 55:1014
30. Chaudry M, Dash KC, Kamienska-Piotrowicz E, Kinjo Y, Persson I (1994) J Chem Soc Faraday Trans 90:2235