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Use of the 1,1′-dimethylferrocene oxidation process for the calibration of the reference electrode potential in organic solvents immiscible with water

Jan Langmaier, Antonín Trojánek, Zdeněk Samec *

J. Heyrovský Institute of Physical Chemistry of the ASCR, v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic

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Abstract

Cyclic voltammetric oxidation of 1,1′-dimethylferrocene (DMFc) at an Au disc electrode in dichloromethane, 1,4-dichlorobutane, 1,6-dichlorohexane, chlorobenzene, 1,2-dichlorobenzene, 1,2-dichloroethane, 2-nitrophenyl octyl ether and nitrobenzene is used to estimate the standard potential E^0(SHE) of the DMFc$^+$/DMFc redox system vs. the standard hydrogen electrode in these solvents. Results indicate that E^0(SHE) tends to decrease a little with the increasing solvent permittivity probably due to a stabilization of the oxidized ferrocene form by its interaction with polar solvent molecules. Estimated values of E^0(SHE) and Au electrode voltammetry of DMFc are then used to calibrate the potential of the bis(triphenylphosphoranylidene)ammonium$^+$ (BTPPA$^+$) ion-selective type reference electrode (RE), which has been often employed in polarization studies at the interface between two immiscible electrolyte solutions. It is shown that when BTPPA$^+$ is present in the form its chloride salt, the reference potential comprises the mixed potential difference due to the balance of currents corresponding to the co-extraction of the BTPPA$^+$ and Cl$^-$ ions into the organic solvent phase of RE. Calibration is verified by measuring the values of E^0(SHE) for the parent ferrocene and two other ferrocene derivatives, *n*-butylferrocene and decamethylferrocene, which are found to agree well with literature data.

Keywords: Ferrocene; Au electrode voltammetry; ITIES; Ion-selective type reference electrode; Reference electrode potential; Calibration

1. Introduction

Polarization measurements at the interface between two immiscible electrolyte solutions (ITIES) have been frequently performed with the galvanic cell, which can be represented by the scheme

$$\mathrm{Ag|AgCl|SCl(w)|SY(o)|RX(w')\|LiCl(w'')|AgCl|Ag'}, \qquad (1)$$

where w (w′,w″) and o denote the aqueous and the organic solvent phase, respectively, SCl, RX and SY stand for the electrolytes dissolved, and the double vertical bar represents the w|w liquid junction in which the liquid junction potential is assumed to be eliminated [1]. The ion-selective type reference electrode (RE) on the organic solvent side of the cell is a combination of the conventional aqueous reference electrode (here a silver–silver chloride electrode) and the reference w|o interface. When a three- [2] or four-electrode potentiostatic system [3] is used for the polarization of the w′|o interface ensuring that no electric current flows through the reference w|o interface, the equilibrium reference potential difference $\Delta_{\mathrm{o}}^{\mathrm{w}}\phi_{\mathrm{ref}} = \phi(\mathrm{w}) - \phi(\mathrm{o})$ is the distribution potential [4] resulting from the multi-ion partition equilibrium (here involving the ions S$^+$, Cl$^-$ and Y$^-$). This potential depends on the standard Gibbs energies of ion transfer from the phase w to the phase o, $\Delta G_{\mathrm{tr,i}}^{0,\mathrm{w}\to\mathrm{o}}$, on the ratio of ion (or salt) concentrations in the phases w and o [5] and, as the case may be, on the ratio *r* of the volumes of the two phases [6]. In practice, the reference ITIES is formed inside the Luggin capillary connected to the phase

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* Corresponding author. Tel.: +420 266052017; fax: +420 286582307.
E-mail address: zdenek.samec@jh-inst.cas.cz (Z. Samec).

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o, where the potential difference $\Delta_o^w\phi_{ref}$ can fast establish, provided that the equilibrium ion concentrations in the phases w and o are practically equal to initial (analytical) ones. Otherwise, the balance of the extraction ion currents gives rise to the mixed potential difference [7], which can vary with time until the partition equilibrium is reached.

Thermodynamic analysis [5] (see also Ref. [8]) suggests that the equilibrium value of the potential difference $\Delta_o^w\phi_{ref}$ can be related to the ratio of the initial concentrations c^o_{SY} and c^w_{SCl} of the salts SY and SCl in the phases o and w, respectively, through the Nernst equation, on condition that $r \approx 1$ and the inequalities $\Delta_o^w\phi^{0'}_{Cl^-} \ll \Delta_o^w\phi^{0'}_{S^+} \ll \Delta_o^w\phi^{0'}_{Y^-}$ are fulfilled, where $\Delta_o^w\phi^{0'}_i$ is the formal ion transfer potential for the ion i. By taking into account the ion association in the phase o and by neglecting the ion association in the phase w, $\Delta_o^w\phi_{ref}$ can be expressed by

$$\begin{aligned}\Delta_o^w\phi_{ref} &= \Delta_o^w\phi^0_{S^+} + \frac{RT}{F}\ln\frac{\alpha\gamma^o_{S^+}c^o_{SY}}{\gamma^w_{S^+}c^w_{SCl}}\\ &= \Delta_o^w\phi^{0'}_{S^+} + \frac{RT}{F}\ln\frac{\alpha c^o_{SY}}{c^w_{SCl}},\end{aligned} \tag{2}$$

where $\Delta_o^w\phi^0_{S^+}$ is the standard ion transfer potential for S^+, $\gamma^{w(o)}_{S^+}$ is the ion activity coefficient, and α is the degree of dissociation of SY in o. In such a case, the reference potential difference $\Delta_o^w\phi_{ref}$ is practically controlled by the equilibrium partition of the S^+ ion. In order to ensure a wide polarized potential window (ppw) at the w′|o interface, the supporting electrolyte SY is typically composed of highly hydrophobic ions with a rather negative $\Delta_o^w\phi^{0'}_{S^+}$ and a rather positive $\Delta_o^w\phi^{0'}_{Y^-}$ However, when the value of $\Delta_o^w\phi^{0'}_{S^+}$ is too negative, the inequality $\Delta_o^w\phi^{0'}_{Cl^-} \ll \Delta_o^w\phi^{0'}_{S^+}$ may not be fulfilled. The problem could be circumvented by using a junction-free RE [9,10].Apparently, the calibration of the ion-selective type RE in the cell (1) is of practical importance. The common procedure is based on the voltammetric measurement of a semi-hydrophobic ion transfer of the known formal ion transfer potential $\Delta_o^w\phi^{0'}$, e.g. tetraethylammonium cation, which is then being used to assess the reference potential from the measured reversible half-wave potential [1]. An alternative calibration could be based on the solid-electrode voltammetry of the ferricenium$^+$/ferrocene (Fc^+/Fc) redox system, which has been recommended as a suitable reference for reporting electrode potentials in nonaqueous solvents including those immiscible with water [10–13]. This recommendation was supported by experimental data indicating that the effect of solvent on the standard electrode potential of the Fc^+/Fc redox couple is rather small [12]. So far, this approach has not been used in electrochemistry at ITIES, though in several studies [14–16] the formal Fc^+/Fc redox potential has been evaluated from voltammetric measurements at a solid electrode for the purpose of estimation of the standard Gibbs energy of electron transfer across ITIES.

The aim of this study was to examine the 1,1′-dimethylferrocene (DMFc) oxidation process for a calibration of the ion-selective type RE in the cell (1). Compared to the parent Fc, its substituted derivatives appear to be more suitable electron donors for electron transfer reactions at ITIES [15]. Therefore, DMFc was chosen to explore also the solvent effect on its standard redox potential. In a number of studies at ITIES, the cell potential has been referred to the tetrabutylammonium$^+$ (TBA^+) or bis(triphenylphosphoranylidene)ammonium$^+$ ($BTPPA^+$) ion-selective type RE. Available thermodynamic data for TBA^+ and Cl^- [17–25] indicate that the reference potential is controlled by the equilibrium partition of TBA^+ between water and any of the organic solvent immiscible in water. On the other hand, no thermodynamic data are available for the $BTPPA^+$ cation. Hence, our strategy was to employ the cell with TBA^+ ion-selective type RE to evaluate first the standard potential of the $DMFc^+$/DMFc redox system for a series of organic solvents, and then to use these data to calibrate the $BTPPA^+$ ion-selective type RE.

2. Experimental

2.1. Chemicals

Organic solvents dichloromethane (DCM, 99.6%, Aldrich), 1,4-dichlorobutane (1,4-DCB, 97%, Aldrich), 1,6-dichlorohexane (1,6-DCH, 98%, Aldrich), chlorobenzene (CB, 99.9%, Aldrich), 1,2-dichlorobenzene (*o*-DCB, 99%, Aldrich), 1,2-dichloroethane (>99.5%, Fluka), 2-nitrophenyl octyl ether (Selectophore®, Fluka) and nitrobenzene (>99.5%, Fluka) were used as received. Supporting electrolytes bis(triphenylphosporanylidene)ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl) and tetrabutylammonium tetrakis(4-chlorophenyl)borate (TBATPBCl) were prepared by metathesis from potassium tetrakis(4-chlorophenyl)borate (KTPBCl, Fluka) and bis(triphenylphosporanylidene)ammonium chloride (BTPPACl, Fluka) or tetrabutylammonium chloride (TBACl, Fluka), respectively, in acetone. Ferrocene (Fc, 98%), 1,1′-dimethylferrocene (DMFc, 97%) and decamethylferrocene (DCMFc, 97%) were purchased from Sigma–Aldrich; *n*-butylferrocene (BuFc, 97%) was purchased from Strem. Aqueous electrolyte solutions were prepared from highly purified water (Millipore).

2.2. Cyclic voltammetry

Voltammetric measurements were carried out at the ambient temperature (25 ± 1 °C) in a conventional all-glass cell by using a three-electrode potentiostat (EG&G PAR, model 273A equipped with M270 software). Au disc electrode (1 mm in diameter), a platinum wire, and the ion-selective type RE served as the working, auxiliary and reference electrode, respectively. The cell can be represented by the scheme

$$\mathrm{Ag|AgCl|0.01\,M\,SCl(w)|5\,mM\,SY + 1\,mM\,DMFc(o)|Au,} \tag{3}$$