

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

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Abstract

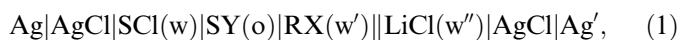
Cyclic voltammetric oxidation of 1,1'-dimethylferrocene (DMFc) at an Au disc electrode in dichloromethane, 1,4-dichlorobutane, 1,6-dichlorohexane, chlorobenzene, 1,2-dichlorobenzene, 1,2-dichloroethane, 2-nitrophenyl octyl ether and nitrobenzene is used to estimate the standard potential $E^0(\text{SHE})$ of the $\text{DMFc}^+/\text{DMFc}$ redox system vs. the standard hydrogen electrode in these solvents. Results indicate that $E^0(\text{SHE})$ 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 $E^0(\text{SHE})$ 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 $E^0(\text{SHE})$ for the parent ferrocene and two other ferrocene derivatives, *n*-butylferrocene and decamethylferrocene, which are found to agree well with literature data.

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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



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 $\Delta\phi_{\text{ref}}^{\text{w}} = \phi(\text{w}) - \phi(\text{o})$ 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, $\Delta G_{\text{tr},i}^{0,\text{w}\rightarrow\text{o}}$, 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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o, where the potential difference $\Delta_o^w \phi_{\text{ref}}$ 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 $\Delta_o^w \phi_{\text{ref}}$ can be related to the ratio of the initial concentrations c_{SY}^o and c_{SCI}^w of the salts SY and SCI in the phases o and w, respectively, through the Nernst equation, on condition that $r \approx 1$ and the inequalities $\Delta_o^w \phi_{\text{Cl}^-}^{o'} \ll \Delta_o^w \phi_{\text{S}^+}^{o'} \ll \Delta_o^w \phi_{\text{Y}^-}^{o'}$ are fulfilled, where $\Delta_o^w \phi_i^{o'}$ 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, $\Delta_o^w \phi_{\text{ref}}$ can be expressed by

$$\begin{aligned} \Delta_o^w \phi_{\text{ref}} &= \Delta_o^w \phi_{\text{S}^+}^o + \frac{RT}{F} \ln \frac{\alpha \gamma_{\text{S}^+}^o c_{\text{SY}}^o}{\gamma_{\text{S}^+}^w c_{\text{SCI}}^w} \\ &= \Delta_o^w \phi_{\text{S}^+}^{o'} + \frac{RT}{F} \ln \frac{\alpha c_{\text{SY}}^o}{c_{\text{SCI}}^w}, \end{aligned} \quad (2)$$

where $\Delta_o^w \phi_{\text{S}^+}^o$ is the standard ion transfer potential for S^+ , $\gamma_{\text{S}^+}^{w(o)}$ is the ion activity coefficient, and α is the degree of dissociation of SY in o. In such a case, the reference potential difference $\Delta_o^w \phi_{\text{ref}}$ 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 $\Delta_o^w \phi_{\text{S}^+}^{o'}$ and a rather positive $\Delta_o^w \phi_{\text{Y}^-}^{o'}$. However, when the value of $\Delta_o^w \phi_{\text{S}^+}^{o'}$ is too negative, the inequality $\Delta_o^w \phi_{\text{Cl}^-}^{o'} \ll \Delta_o^w \phi_{\text{S}^+}^{o'}$ 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 $\Delta_o^w \phi^{o'}$, 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 ferricinium⁺/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.

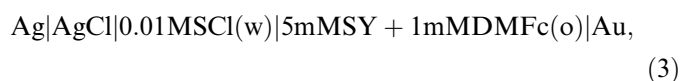
2. Experimental

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(triphenylphosphoranylidene)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(triphenylphosphoranylidene)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



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