



Some aspects of impedance measurements at the interface between two immiscible electrolyte solutions in the four-electrode cell

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ABSTRACT

Electrochemical impedance spectroscopy (EIS) was used to study the impedance behaviour of a macroscopic water/1,2-dichloroethane (DCE) interface (0.32 cm^2) in a four-electrode cell. Impedance measurements were carried out at the equilibrium electrical potential difference controlled by the partition of the tetraethylammonium (TEA^+) ion present in both phases. Impedance data could be fitted to a two-terminal electrical equivalent circuit (EEC) consisting of the Randles EEC with a stray capacitance in parallel, and a stray resistance in series. The change in the distance between the organic reference electrode tip and the interface had only little effect on the value of the double layer capacitance, Warburg impedance and kinetic resistance, unless this distance was extremely short so that the shielding errors causing non-uniform current densities could not be safely avoided. The analysis provided the apparent standard rate constant of the TEA^+ ion transfer of about 0.1 cm s^{-1} , which agrees well with the results of the previous equilibrium EIS measurements on both macroscopic and microscopic interfaces, but disagrees with those of the steady-state (non-equilibrium) voltammetric measurements on the nanoscopic interfaces. The four-terminal EEC including the impedances of the organic reference and counter electrodes, as well as the impedances of the parasitic coupling between the counter and reference electrodes, allowed simulating the experimental impedance behaviour over the whole range of frequencies of the applied ac voltage (1 Hz–100 kHz).

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1. Introduction

Electrochemical impedance spectroscopy (EIS) has been used to study the faradaic and non-faradaic processes at the interface between two immiscible electrolyte solutions (ITIES) since 1974 [1], cf. the recent reviews [2–4]. Typically, the impedance measurements at the ITIES have been performed using a four-electrode cell with two reference electrodes (RE1, RE2) and two counter electrodes (CE1, CE2) [5]. However, the interpretation of the impedance data has been often complicated by the artefacts arising from the high impedances of the reference and counter electrodes and from the parasitic coupling between the electrodes [6], as well as from the inadequate impedance matching of the electrodes and the potentiostat inputs [7]. These effects are very similar to those encountered in the three-electrode impedance measurements at solid electrodes [8,9].

The common problem of the electrochemical measurements at the ITIES is the effect of the uncompensated ohmic potential drop due to the electrolyte resistance between the reference electrodes and the interface, which introduces a potential control error. In EIS, the solution resistance can be evaluated by fitting the impedance data to an equivalent electrical circuit consisting of the ohmic resistance in series to the parallel combination of the double layer capacitance and the faradaic impedance (Randles-type circuit) [10]. However, such fit becomes tricky when the parasitic elements influence significantly the impedance behaviour [9]. In general, the reduction of the solution resistance should allow both increasing the accuracy of evaluation of the kinetic resistance and suppressing the effects of the parasitic elements.

The aim of this work was to investigate the impedance behaviour of the water/1,2-dichloroethane (DCE) interface at the equilibrium electrical potential difference controlled by the partition of the tetraethylammonium (TEA^+) ion present in both phases. We intended to clarify the effects of the solution resistance and the parasitic elements of the four-electrode cell on the kinetic analysis of the ion transfer across the ITIES. We shall show that the reduction of the solution resistance by means of decreasing the

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distance between the organic reference electrode tip and the interface has in fact only little effect on the evaluation of both the transport and kinetic parameters of the ion transfer, as well as the double layer capacitance. We shall also show that the impedance behaviour of this system can be simulated using a four-terminal equivalent electrical circuit [6] including the impedance of the organic reference and counter electrodes, as well as the impedances of the parasitic coupling elements between the counter electrodes CE1 and CE2, and the reference electrodes RE1 and RE2.

2. Experimental

LiCl, tetraethylammonium chloride (TEACl), tetrabutylammonium chloride (TBACl), sodium tetrphenylborate (NaTPB), and tetrabutylammonium tetrphenylborate (TBATPB) were purchased as analytical grade chemicals from Sigma-Aldrich and used as received. TEATPB was prepared from TEACl and NaTPB by metathesis and purified by recrystallization from acetone. Organic electrolyte solutions were prepared from 1,2-dichloroethane (puriss, p.a.), which was purchased from Fluka and used as received. Aqueous electrolyte solutions were prepared from highly purified water (Millipore).

The scheme of the four-electrode cell, which was a modification of the previous cell design [11], is shown in Fig. 1. A flat water/1,2-DCE interface (0.32 cm^2) was formed in the round hole of the glass barrier between the two liquid phases. The position of the tip of the Luggin capillary of the organic reference electrode RE1 could be adjusted to the desired distance d from the interface ($d \sim 0.2$ – 3.0 mm), which was measured optically. The cell was immersed in a water bath, the temperature of which was maintained at 298 K. The cell can be represented by the scheme:

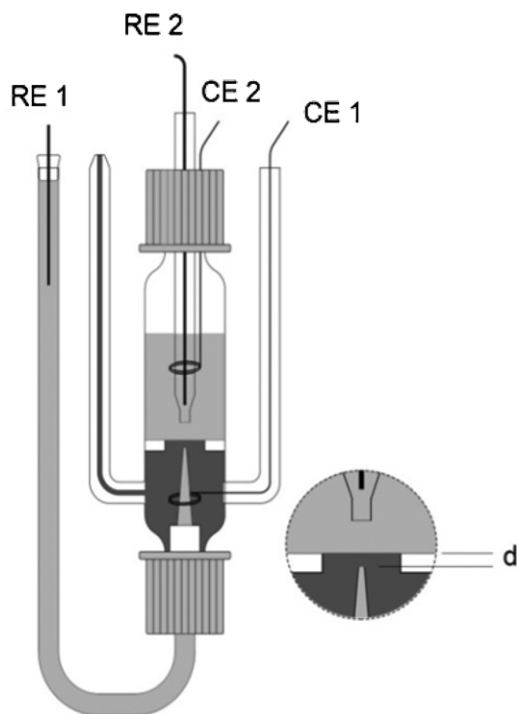


Fig. 1. Scheme of the four-electrode cell with the reference electrode RE 1 and the counter electrode CE 1 connected to the organic solvent phase (dark grey area), and the reference electrode RE 2 and the counter electrode CE 2 connected to the aqueous phase (light grey area). The distance d between the interface and the tip of the Luggin capillary for the organic reference electrode RE1 is adjustable from ca. 0.2 mm to 3.0 mm; the latter value represents the thickness of the glass barrier.

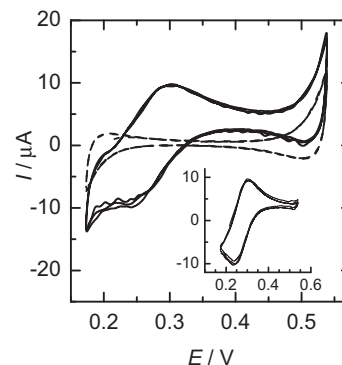


Fig. 2. Three succeeding cyclic voltammograms (CVs) of the TEA^+ ion transfer across the water/1,2-DCE interface (solid lines) and the supporting electrolyte current (dashed line) measured at 5 mV s^{-1} without the ohmic potential drop compensation in the Cell I ($x=0$, $y=0.5$, $d=1 \text{ mm}$, solution resistance 500Ω). Inset: the CVs corrected for the supporting electrolyte current.

$\text{Ag}^+|\text{AgCl}|0.1 \text{ M TBACl} (w')|0.05 \text{ M TBATPB} + x \text{ mM TEATPB} (o)|0.05 \text{ M LiCl} + y \text{ mM TEACl} (w)|\text{AgCl}|\text{Ag} (\text{Cell I})$

where $x, y = 0.0 - 0.5$.

Voltammetric and impedance measurements were carried out using Solartron ModuLab System (Solartron Analytical, Ametek). Impedance plots were fitted to an equivalent electrical circuit using the ZView 3.3b software (Scribner Associates, Inc), and simulated using Mathcad 15.0 software (PTC).

3. Results and discussion

3.1. Cyclic voltammetry of the TEA^+ ion transfer

Cyclic voltammetry was used to determine the value of the reversible half-wave potential for the TEA^+ ion transfer on the present potential scale, which presumably should equal to the reversible potential (open circuit potential) of the Cell I at equal concentrations of TEA^+ in both the aqueous and organic solvent phase ($x=y$). Fig. 2 shows the cyclic voltammograms (CVs) of the TEA^+ ion transfer across the water/1,2-DCE interface recorded without any ohmic potential drop compensation. A correction for the supporting electrolyte current (dashed line) gives the CVs shown in the inset, which can be characterized by the mid-point potential $E_m = 0.270 \text{ V}$. The latter value is close to the value of the reversible half-wave potential $E_{1/2}^{\text{rev}} = 0.280 \text{ V}$, as

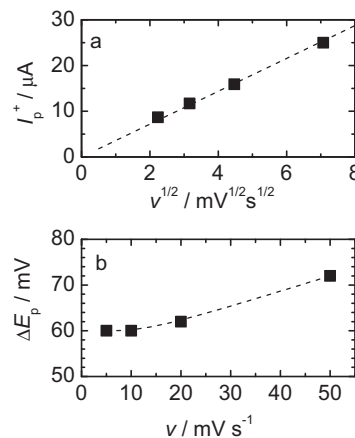


Fig. 3. Effect of the sweep rate ν on the positive peak current I_p^+ (panel a) and the peak potential difference ΔE_p (panel b) measured without the ohmic potential drop compensation in the Cell I ($x=0$, $y=0.5$, $d=1 \text{ mm}$, solution resistance 500Ω).

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