



## Three-phase electrochemistry. Influence of temperature on ion transfer

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### ABSTRACT

A study on the influence of temperature and time on ion transfer across the liquid|liquid interface is reported. Three anions of different hydrophobic properties were selected for the examination:  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ . It was found that while the current magnitudes of the oxidation of dmfc in NB in the presence of selected anions in water are very different at room temperature, they become comparable above 45 °C. This finding indicates that the ability of the examined anions to reach significant concentrations in the organic phase, at 45 °C, becomes similar. For the anions of lower affinity to the organic phase ( $\text{NO}_3^-$  and  $\text{Cl}^-$ ), distinct current oscillations appeared in the recorded experimental voltammograms and amperograms.

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### 1. Introduction

Three-phase electrochemistry or three-phase electrodes are employed in several fields of electrochemistry and electroanalysis [1–6]. One of the interesting aspects of three-phase electrochemistry is the investigation of ion transfer across the phase boundary and of the electrode reactions that require such a transfer of ions. The electrochemical examination of ion transfer across the liquid|liquid interface started with the four-electrode arrangement [7], however, due to serious limitations of that setup, the four-electrode system has been replaced with the three-electrode one.

Marken et al. [8–10] deposited an oily electroactive compound in the form of several droplets on the graphite electrode surface and in such a way a three-phase junction – electrode/organic phase/aqueous phase was formed. Scholz et al. [11–13] replaced the oxidation of pure organic phase with the oxidation of an electroactive compound in different organic solvents. In their approach a droplet of organic liquid with dissolved hydrophobic electroactive compound was attached to the graphite electrode surface. The electrode was immersed in an aqueous solution containing various inorganic salts. Opallo and coworkers used electrodes based on hydrophobic porous silicate matrix and homogeneously dispersed electrode conductor (graphite particles) [14–16]. Such electrodes were easily impregnated with hydrophobic organic non-polar solvents. Similarly as before, the transfer of ions was related to their lipophilicity and thus could be monitored as a function of electrode potential. Li et al. [17] have shown that

micro- and nanopipettes are very useful in studying the transport of uncharged and charged species at the water/1,2-dichloroethane interface with low concentrations of or without supporting electrolyte. We have proposed a new three-electrode setup [18] in which the graphite rod was replaced with a very thin gold or platinum wire which was placed in a mixture of two immiscible liquids in such a way that the upper part of the wire remained in the aqueous phase and its lower part was totally immersed in organic liquid. The proposed configuration provides reproducible and well defined and controllable length of three-phase boundary. The organic phase can be also represented by a drop dispensed from a capillary [19]. By applying the microcylindrical approach and an electropolymerization process it was possible to examine how deeply the particular anions can penetrate the organic phase [20].

Other recent developments in the three-phase electrochemistry include: (1) the finding that for very hydrophilic anions the cationic product may be transferred from the organic phase to water [21], and (2) for prolonged electrolysis times the precipitation of the dmfc cation with the corresponding anion may take place [22].

Since a change in temperature and prolonged electrolysis time may affect substantially the ion ability to exist in the organic phase at higher concentrations, we demonstrate in this paper, how temperature and time affects the process of ion transfer in three-phase electrochemistry.

### 2. Experimental

Voltammetric measurements were performed in the three-electrode system using an AUTOLAB, model PGSTAT 30, potentiostat

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(Eco-Chemie, Utrecht, The Netherlands). A special thermostated voltammetric cell has been constructed for the measurements. A platinum cylindrical electrode of 300  $\mu\text{m}$  in diameter served as the working electrode. A silver/silver chloride/saturated KCl ( $E = 0.199\text{ V}$  vs. NHE) was used as the reference electrode and a platinum wire was the auxiliary electrode. The organic phase in form of a drop was dispensed from a capillary with the help of a precision dispenser. The cell was enclosed in a Faraday cage to minimise the electrical noise.

Lithium perchlorate ( $\text{LiClO}_4$ ), sodium chloride ( $\text{NaCl}$ ) and lithium nitrate ( $\text{LiNO}_3$ ) were of high purity (pure p.a.) and were purchased from Fluka. Decamethylferrocene and nitrobenzene were purchased from Aldrich.

A detailed description how a platinum microwire can be immersed partially into a nitrobenzene drop and partially in the aqueous phase can be found in [19].

### 3. Results and discussion

In one of our previous papers [22] we have found that under some conditions decamethylferrocenium salts may precipitate in the solution. Such precipitation must affect immediately local conductivity in the organic phase, so we thought it might trigger the appearance of oscillations in the measured current. Since, it is known that solubility of chemical compounds and the mass-transport rate are usually strongly temperature dependent, we have decided to examine the dmfc electrode processes in a wider time range and at different temperatures compared to earlier papers. It appeared that in the case of anions of more positive transfer potentials (more hydrophilic) and, consequently, of limited ability to move into the organic phase, current oscillations indeed can be seen in the measured responses. For  $\text{NO}_3^-$  and  $\text{Cl}^-$  these oscillations were found in both: cyclic voltammograms and chronoamperometric transients.

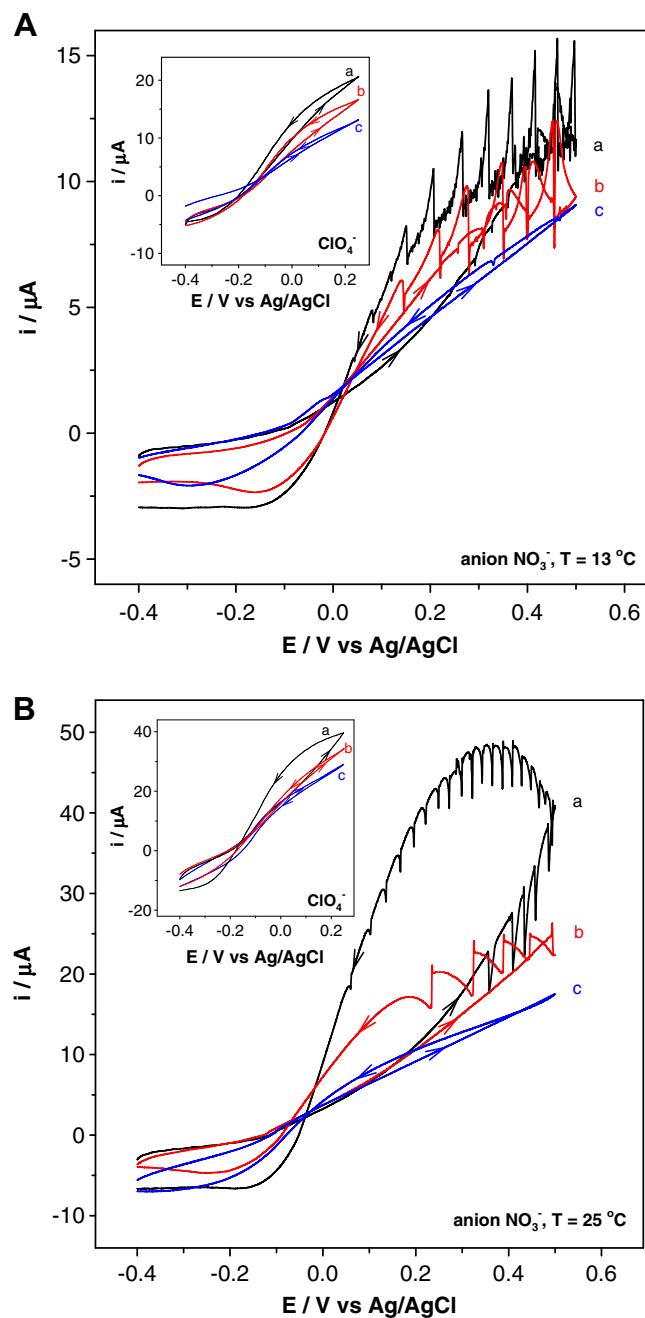
In the case of  $\text{NO}_3^-$  the oscillations were observed in cyclic voltammograms in the entire investigated temperature range, i.e. from 13 to 55  $^\circ\text{C}$ . Exemplary cyclic voltammograms of decamethylferrocene obtained in the presence of  $\text{LiNO}_3$  in the aqueous phase at two selected temperatures (13 and 25  $^\circ\text{C}$ ) are shown in Figs. 1A and B. At small scan rates (longer experimental times), for both selected temperatures, the oscillations appear earlier and usually have larger amplitudes (see curves a in Figs. 1A and B). At higher scan rates the oscillations are not seen in the first several scans (see curves c) and appear eventually in consecutive scans. Interestingly, when  $\text{ClO}_4^-$  was present in the aqueous phase, no current oscillations were observed at any temperature; see the insets in Fig. 1A and B. In chronoamperometry, the appearance of the oscillations ( $\text{NO}_3^-$ ) is preceded by a delay time of ca. 100 s. Once the oscillations appear they maintain their frequency at a rather constant level. For the explanation of the hysteresis in the voltammograms see Ref. [22].

Cyclic voltammograms obtained in the presence of the chloride ions in the aqueous phase also exhibit the oscillations. There are, however, some differences: at lower scan rates the magnitude of oscillations is smaller compared to nitrates and oscillations disappear at temperatures higher than 45  $^\circ\text{C}$ .

At low dmfc concentrations the oscillations appeared for none of the examined anions.

#### 3.1. Dependence of current on temperature

The influence of temperature on the magnitudes of the oxidation peak currents of decamethylferrocene was investigated in the presence of three selected anions ( $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$ ) in the aqueous phase. The selected anions represent different abilities



**Fig. 1.** Cyclic voltammograms for 0.05 M decamethylferrocene obtained with the 300- $\mu\text{m}$  Pt microcylindrical electrode. Depth of penetration of nitrobenzene drop: 1500  $\mu\text{m}$ . Aqueous phase – 1 M  $\text{LiNO}_3$ ; scan rate: 2 (a), 5 (b) and 20 mV/s (c); temperature: 13  $^\circ\text{C}$  (A) and 25  $^\circ\text{C}$  (B). Inset: aqueous phase – 1 M  $\text{LiClO}_4$ ; all other conditions as in A and B.

to move into the organic phase. The examined temperature range could not be too wide, since at high temperatures the mutual solubility of water and nitrobenzene significantly increases. For example, a temperature increase from 20 to 60  $^\circ\text{C}$  is related to an increase in the solubility of water in nitrobenzene from 0.24% to 0.7% m/m, and of nitrobenzene in water from 0.19% to 0.4% m/m [23]. In the temperature measurements the main emphasis was put on more hydrophilic anions like  $\text{NO}_3^-$  and  $\text{Cl}^-$ , however; we started with  $\text{ClO}_4^-$  which is the most hydrophobic among the examined anions, enters well the organic phase [24] and therefore was expected to give simple, linear Arrhenius-like ( $\ln i$  vs.  $1/T$ ) dependencies. Reliable activation-energy data cannot be obtained from these dependencies, since the rate-limiting process is unknown.

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