

# Three-phase electrochemistry with cylindrical microelectrode crossing vertically the boundary of two immiscible liquids

Elzbieta Bak, Mikolaj Donten, Zbigniew Stojek \*

*Department of Chemistry, Warsaw University, ul. Pasteura 1, PL-02-093 Warsaw, Poland*

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## Abstract

We report on a new experimental method for investigation of ion transfer across the boundary of two immiscible liquids. The first report on this method has been published in *Electrochemistry Communications* [E. Bak, M. Donten, Z. Stojek, *Electrochem. Commun.* 7 (2005) 483]. This paper is a result of substantial expansion of the above communication. The key idea of the new method is immersing a cylindrical, platinum or gold microelectrode into a two-liquid system in such a way that one part of the microelectrode is located in one liquid and the second part resides in the second liquid. The organic liquid contains a hydrophobic depolarizer and, importantly, no supporting electrolyte. The aqueous phase contains appropriately selected ionic compounds. The dependence of the formal potential derived from the square-wave voltammograms of decamethylferrocene vs. the standard potential of transfer of the anions present in the aqueous phase was perfectly linear. Therefore, this dependence can be used for the determination of new standard-potential-of-ion-transfer values. The developed method is more precise than the other methods, since the three-phase boundary formed with a metallic wire is better defined and better reproduced compared to placing a drop of organic liquid on the surface of a graphite electrode. The new method should be applicable to a larger set of organic liquids. It is also useful for the examination of the reaction layer width in the organic phase. © 2006 Elsevier B.V. All rights reserved.

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## 1. Introduction

At present we face an increasing interest in three-phase electrochemistry. Three-phase electrochemistry involves the use of three phases, which are in contact. The first phase is the conducting electrode material and two other phases are liquids that are immiscible. During the electrode process the ions cross the boundary between the two liquid phases. Usually one of them is organic and the other one aqueous. In the traditional approach to examination of ion transfer, the experimental setup involves a four-electrode arrangement (two reference- and two counter electrodes) [1]. However, its applicability is limited only to

polarizable phase boundaries, at which, in turn, relatively narrow potential ranges are available.

Recently, a new approach, free from the above limitations, has been developed [2–9]. In this new approach the four-electrode system has been replaced with a three-electrode one. The most important element in this arrangement is a graphite rod, which is brought in a direct contact with two immiscible liquid phases; organic solvent droplet is attached to the graphite disc surface, which, in turn, is immersed into the aqueous phase. Along the circumference of the droplet a three-phase junction is formed. Only there the electrochemical reaction can start and advance into the organic solvent droplet. This was experimentally proved by monitoring the electrode-reaction products with a microelectrode probe immersed into the oil droplet [10].

The above approach was proposed simultaneously and developed independently by several authors. Marken

\* Corresponding author. Tel.: +48 22 822 0211; fax: +48 22 822 4889.  
E-mail addresses: [donten@chem.uw.edu.pl](mailto:donten@chem.uw.edu.pl) (M. Donten), [stojek@chem.uw.edu.pl](mailto:stojek@chem.uw.edu.pl) (Z. Stojek).

et al. [2–4] deposited an oily electroactive compound in the form of several droplets on the graphite electrode surface. After that, the electrode was immersed into aqueous solutions of different inorganic salts. Voltammetric oxidation of the electroactive oil was accompanied by insertion of anions from the aqueous to the organic phase and occurred at potentials that depended on the hydrophilic properties of the incorporated counterions. Scholz et al. [5–8] used highly hydrophobic paraffin-impregnated graphite electrodes (PIGE). They replaced pure organic phase with a solution of an electroactive compound in different organic solvents, e.g. nitrobenzene [5–7], *n*-octanol [11], 2-nitrophenyloctyl ether [12] and *L*- and *D*-menthol melts [13] and were able to determine standard Gibbs energies of transfer of a number of anions and cations. A droplet of organic liquid with a dissolved hydrophobic electroactive compound was attached to the graphite electrode surface. The electrode was immersed in the aqueous solution containing various inorganic salts. The transfer of ions across the phase boundary was triggered by either electrooxidation or electroreduction of the compound dissolved and “trapped” in the organic liquid.

In another approach, Shi and Anson [14–16] covered the electrode with a thin layer of, e.g., nitrobenzene, in which electroreactant was dissolved. In the case of nonpolar organic solvents an electrolyte was added to reduce the ohmic potential drop within the layer. This solution resembled the four-electrode approach to some extent.

Opallo and coworkers [17–20] encapsulated the organic phase in a ceramic carbon material composed of carbon particles and hydrophobic silicate. It was prepared via the sol-gel chemistry from methyltrimetoxysilane-based sol. Similarly as before, the transfer of ions was related to their lipophilicity and thus could be monitored as a function of electrode potential. They have also examined the transfer of ions through an ionic liquid–aqueous solution interface [21].

Li and coworkers [22] demonstrated that micro- and nano-pipettes 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. The paper clearly shows the influence of migration effect on the ion transfer at liquid/liquid interface of two immiscible solvents.

Lately, we have proposed a new electrochemical setup [23], which represents further development of the above three-electrode system. Graphite rod was replaced with a thin gold or platinum wire, which played a role of microcylindrical working electrode. It 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 immersed in the organic liquid. The proposed configuration provides reproducible and well defined length of the three-phase boundary (determined by the stable diameter of the wire), which results in a much better reproducibility of the magnitudes of the measured current responses. Moreover, the length of the three-phase junction

can be easily controlled by appropriately changing the metal wire diameter. In addition, there is a possibility of employing various electrode materials.

This paper, compared to the earlier communication, describes more objects and more data on the electrochemistry at the three-phase boundary with the use of a cylindrical microelectrode. Special emphasis is given to the thickness of the reaction layer at the phase boundary and to its expansion in time.

## 2. Experimental

Voltammetric measurements were performed in the three-electrode system using an EG&G PARC, model 273 potentiostat that was controlled via personal computer. The voltammetric cell was of special design to allow the introduction of nitrobenzene to the cell from the bottom through a thin capillary and to keep the liquid interface move slowly upwards. Under these conditions the immobilized microcylinder electrode was made smoothly enter the interface. The interface was very well-defined and the surface of the two-phase boundary was always vertical to the microcylinder. This procedure limited a possibility of contamination of the organic phase with microdroplets of water. Platinum cylindrical electrodes of 50, 100, 200, 300, 500 and 800  $\mu\text{m}$  in diameter and gold cylindrical electrodes of 100, 200, 300 and 500  $\mu\text{m}$  in diameter served as the working electrodes. The length of the working microwires was ca. 10 mm, however, importantly, the microwire length did not affect the magnitude of the measured current. The wire was immersed into the system in such a way that each liquid phase contained ca. 50% of it. A change in this proportion changed the capacitive currents and did not change the faradaic currents. A silver/silver chloride/saturated KCl electrode ( $E = 0.199$  V versus SHE) was used as the reference electrode and a platinum wire was the auxiliary electrode. Pt quasi-reference electrodes were used in the cases where the knowledge of the wave potential was not important. The cell was enclosed in a Faraday cage to minimize electrical interferences.

Typical instrumental parameters for square-wave voltammetry (if not specified elsewhere) were the following: SW frequency of the potential modulation,  $f$ : 10 Hz, SW height of the potential pulses,  $E_{\text{SW}}$ : 50 mV, and potential step of the staircase ramp,  $\Delta E$ : 1 mV.

The chemical reagents: lithium perchlorate ( $\text{LiClO}_4$ , 99%), sodium chloride ( $\text{NaCl}$ ), sodium bromine ( $\text{NaBr}$ ), sodium iodine ( $\text{NaI}$ ), sodium thiocyanate ( $\text{NaSCN}$ ), sodium nitrate ( $\text{NaNO}_3$ ), sodium tetrafluoroborate ( $\text{NaBF}_4$ ), sodium hexafluorophosphate ( $\text{NaPF}_6$ ), sodium tetrphenylborate ( $(\text{C}_6\text{H}_5)_4\text{BNa}$ , 99.5%), sodium trifluoromethanesulfonate ( $\text{CF}_3\text{SO}_3\text{Na}$ , 97%), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) were purchased from Fluka, and were used as supporting electrolytes in the aqueous phase. Ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ , 98%) and dexamethylferrocene were purchased from Aldrich. *N*-vinylcarbazole was purchased from Fluka. Nitrobenzene was supplied by Aldrich. The aqueous elec-

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