

Three-phase electrochemistry with a cylindrical microelectrode

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Abstract

A new experimental approach is proposed to examine the ion transfer across the boundary of two immiscible liquids. A cylindrical platinum or gold microelectrode is immersed into the two-liquid system in such a way that a part of it is located in one liquid and the other part resides in the second liquid. The organic liquid contained either ferrocene or decamethylferrocene and no supporting electrolyte. The aqueous phase contained various inorganic salts. Well defined and reproducible linear-scan and square-wave voltammograms of oxidation of ferrocene and decamethylferrocene were obtained. The dependence of the formal potential derived from the square-wave voltammograms of decamethylferrocene vs. the standard potentials of transfer of anions present in the aqueous phase was perfectly linear. The developed method is more precise, since the three-phase boundary is better defined compared to placing a drop of organic liquid on the surface of a graphite electrode, and should be applicable to a larger set of organic liquids. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The following four terms: three-phase junction, three-phase boundary, three-phase electrode and three-phase electrochemistry and appear frequently in recent electrochemical literature. These expressions are used to report the electrochemical experiments involving a solid electrode in contact with two other phases: either one solid and one liquid or two liquid. Each above case involves the transfer of ions from one phase to another. Example publications reporting on some analytical and physicochemical aspects of electrochemistry of solid particles/phases anchored on the surface of a polarizable electrode and immersed in a solution are the following [1–5]. Abrasive stripping voltammetry belongs to this group [6]. The second case of two liquids in contact with a solid electrode got more attention. Marken et al. [7–9] were the first who noted the importance and consequences of ion transfer from one liquid to another at a

three-phase electrode. They deposited an oily electroactive compound (*N,N,N',N'*-tetrahexylphenylene diamine, THPD) in the form of several droplets on the graphite electrode surface and immersed this composition into aqueous solutions of different inorganic salts. Oxidation of THPD proceeded at voltammetric potentials dependent on the hydrophilic properties of the anions from the aqueous solution.

Scholz et al. [10–14], in a try to measure the lipophilicity of ions, modified and improved the above approach to the two-liquid system. They employed highly-hydrophobic paraffin-impregnated graphite electrodes (PIGE) instead of pyrolytic graphite. Moreover, they replaced the pure organic phase with a solution of selected electroactive compound (e.g., decamethylferrocene) in organic solvents such as nitrobenzene [10–12,15], *n*-octanol [16], and 2-nitrophenyloctyl ether [17]. While the electrode process was limited to the solute, similarly as before, the wave potential depended on the lipophilicity of the anions incorporated into the organic phase. The authors assigned the observed potential shifts to the differences in the Gibbs energies of transfer of the

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ions being transferred across the interface of the two immiscible liquids.

The three-phase electrochemistry approach was a step forward compared to the conventional four-electrode method. The latter was successively applied to the studies on thermodynamics of ion transfer between two immiscible electrolyte solutions (ITIES) [18]. However, the four-electrode method has some limitations. For instance, it is applicable only to organic solvents forming a polarisable interface with water and requires the presence of supporting electrolyte in both phases. The available potential range is narrowed by the transfer potentials of the ions of the added salts; it equals usually 400–600 mV and can be broadened only by either coupling the solution equilibria in both phases [19–21] or by using the microhole arrangement [22,23]. In the three-phase electrode the identification of the ion crossing the liquid/liquid interface is easier and the application of the solvents of rather low dielectric constants, such as *n*-octanol, and *L*- and *D*-menthol melts [16,24,25] is possible.

The unique ability of the three-phase setup arises from the presence of the three-phase junction along the circumference of the droplet attached to the electrode support. Only there the electrochemical reaction can proceed and advance into the organic solvent droplet, regardless of the electrical conductivity of the organic phase. This was experimentally proved by employing a microelectrode probe [26].

It should be mentioned here that ion 'sensitive' voltammograms can be obtained also when a drop of organic liquid is replaced by a thin layer covering partially the electrode surface. This is the case of the paper by Opallo and co-workers [27], who recently instigated the ion transfer across liquid/liquid interfaces of the type: aqueous solution/solution of electroactive compound in polar organic solvent supported on a hydrophobic silicate carbon composite. Shi and Anson [28–30] showed earlier that when a droplet of the organic phase is replaced with a thin film of this solvent (containing dissolved electroreactant) the obtained two-phase electrode becomes analytically applicable. In this experimental arrangement the application of a layer of organic solvent may require the addition of supporting electrolyte, which makes the system similar to the four-electrode one.

Contrary to several advantages arising from the application of the three-phase electrode there are still some problems. The most important ones are the irreproducibility of the droplet size, and the need of using the graphite substrate due to the instability of organic droplets at metal surfaces. Therefore, a new method has been proposed in this paper. In this new method a gold or platinum microcylindrical electrode, instead of an impregnated graphite rod, serves as the working electrode. The cylinder is immersed into the two-phase sys-

tem and is in a direct contact with both immiscible liquids. The electroactive species is dissolved in the organic liquid, while the supporting electrolyte is present only in the aqueous phase. Similarly as before, the oxidation of the substrate is accompanied by the simultaneous incorporation of the respective counterion from the aqueous to the organic phase. The mechanism of charge transfer across the phase boundary is identical to that described in, e.g. [7,10–12,27,28]. Some advantages are clear. The first one is that there is no restriction on the electrode material, since no droplet has to be attached to the electrode surface of particular properties. Moreover, the length of the three-phase junction can be controlled by appropriately changing the metal wire diameter. Due to the constancy of this length, the measured current responses are satisfactorily reproducible and are always proportional to the electrode diameter.

2. Experimental

A special voltammetric cell was constructed. The cell enabled us to use a small volume of the organic liquid (nitrobenzene). Nitrobenzene was added to the cell through a thin capillary and the liquid interface moved slowly upwards. Under these conditions the immobilised microcylinder was smoothly entering the interface. Finally the interface was very well defined and the surface of the two-phase boundary was always vertical to the microcylinder. This procedure helped to stop possible contamination of the organic phase with microdrops of water. A scheme of the cell is presented in Fig. 1(a). Platinum cylindrical electrodes of 50, 100, 200, 300, 500 and 800 μm in diameter and gold cylindrical electrodes of 100, 200, 300 and 500 μm in diameter served as the working electrodes. The length of the working microwires was circa 10 mm, however, the microwire length did not affect the magnitude of the measured faradaic current. The wire was immersed into the system in such a way that each liquid phase contained circa 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 ($E = 0.199\text{ V}$ vs. 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. Only the first voltammograms obtained in newly prepared systems were taken into the analysis, since the consecutive curves differed from the first ones. The measured currents tended to increase. We believe the differences between the consecutive voltammograms were caused by the increase in the concentration of ions in the organic phase.

Voltammetric measurements were performed in the three-electrode system using an EG&G PARC, model 273 potentiostat and controlled via personal computer.

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