Electrochimica Acta 132 (2014) 158–164

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Comparison of Ion Transfer Thermodynamics at Microfluidic and Droplet-Based Three Phase Electrodes

Dawid Kaluza[1], Wojciech Adamiak*,[1], Marcin Opallo[1], Martin Jonsson-Niedziolka**,[1]

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

ARTICLE INFO

Article history:
Received 14 February 2014
Received in revised form 14 March 2014
Accepted 14 March 2014
Available online 5 April 2014

Keywords:
ion transfer
microfluidics
Gibbs energy of ion transfer
liquid-liquid interface
three phase electrode

ABSTRACT

We have investigated whether the thermodynamic model developed for ion transfer processes across the liquid|liquid interface at a droplet-based three phase electrode (TPE) can be applied to a microfluidic system. We have compared effect of ion transfer potential and ion concentration on the voltammetric peak potential recorded at droplet and microfluidic TPEs. The results were analyzed in terms of the Nernst-like equation derived for droplet TPE. As a model reaction, electrooxidation of decamethylferrocene coupled to anion transfer from aqueous electrolyte solution to *N*-octyl-2-pyrrolidone (NOP) has been chosen. We have found that both ion effect and concentration effect are the same in the two systems and agree with the Nernst equation. This allows microfluidic TPEs to be used in electroanalysis. Additionally, Gibbs energies of transfer for different inorganic anions have been determined for the studied NOP water biphasic system.

1. Introduction

Ion transfer processes across liquid interfaces have been intensively studied due to the numerous applications of these processes in chemistry, biology, and pharmacy [1]. For example, they have been used in chemistry for determination of heparin [2], protamines [3] and nucleotides [4]. In biology, their use includes studying biomimetic charge transfers through artificial membranes [5] and designing biocompatible sensors [6]. In pharmacy, they have been utilized for determination of lipophilicity of ionizable drugs [7] and for studying their transfer mechanisms [8].

Generally, ion transfer can be driven chemically or electrochemically. In the first case, the ions are transferred to compensate a charge imbalance formed during a redox reaction at the liquid interface [9–11]. In the second case, two methods can be distinguished. The first one is when the ion transfer is driven by electrostatic polarization of the liquid interface [12–14]. In this method one needs a four electrode setup and large volumes of both liquid phases since each phase contains a pair of counter and reference electrodes. The second case of electrochemically driven ion transfer is when the ions are transferred due to an electrode reaction of electroactive species dissolved in one of the liquid phases, usually the organic phase [15–34]. This method is more advantageous than the former one, because it can be performed in a three electrode setup, it does not require a reference electrode for the organic solution and it operates with smaller volume of the organic phase. In fact, the organic phase volume can be reduced to a micro-droplet deposited on the electrode surface.

Depending on whether the droplet covers the whole electrode surface or not, one can distinguish a thin film electrode (TFE) [15–23] or a three phase electrode (TPE) [24–34]. In the case of TFE, the electrode surface is completely covered by the organic droplet. For this reason, the droplet must contain supporting electrolyte to ensure sufficiently high conductivity to perform electrochemical measurements. This limits the number of solvents that can be used to those of moderate polarity, e.g. nitrobenzene [15–19] or benzonitrile [20–23]. In the case of TPEs, the electrode surface is not covered completely by the organic droplet so an interface exists between the three adjacent phases, i.e. the electrode, the droplet, and the surrounding aqueous phase. The electrode reaction starts at the three phase junction and then propagates towards the center of the droplet [24,25]. For this reason, there is no need of using supporting electrolyte in the organic phase. This is the main advantage of TPEs over TFEs, because it extends the range of organic solvents that can be used to non polar solvents like toluene [26] or alkanes [27–29]. In 2000 Scholz and co-workers developed a thermodynamic model to describe the ion effect and the concentration effect

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* Corresponding author. Tel.: +48 22 343 33 75.
** Corresponding author. Tel. +48 22 343 33 06.
E-mail addresses: wadamiak@ichf.edu.pl (W. Adamiak), martinj@ichf.edu.pl (M. Jonsson-Niedziolka).

[1] ISE member.

http://dx.doi.org/10.1016/j.electacta.2014.03.105
0013-4686/

on the voltammetric peak potentials [30]. The authors derived a Nernst-like equation that has allowed droplet TPEs to be used for determination of transfer energies of different anions [30–33] and cations [34].

Although TPEs are simple and easy to use, the reproducibility of currents is an issue worth to improve, and it is desirable to achieve a stable three-phase electrochemistry even when using metal electrodes. Low reproducibility is because the peak current depends on the length of the three phase junction which is defined by the circumference of the droplet. Since the droplets are deposited by a drop casting method with a micropipette, their circumference is not exactly the same in each experiment. This is reflected by lower reproducibility of the peak currents.

The problem of low reproducibility of the three phase junction length can be overcome by combining TPEs with microfluidic systems under multiphase flow conditions. In 2007 Marken's group showed that a three phase junction exists between co-flowing streams of water and *N*-octyl-2-pyrollidone (NOP) phases on Au band electrode placed at the bottom of the rectangular channel [35]. Electrooxidation of n butylferrocene in NOP was reported to be followed by transfer of ClO_4^- anions from the aqueous phase to NOP. In subsequent studies, NOP was replaced by acetonitrile and the effect of the flow rate on the limiting current was highlighted [36,37]. Recently, our group reported flow rate dependence of the limiting current in a wider range than that examined by Marken's group and we suggested a model for the behavior of the limiting current of TPEs under multiphase flow conditions [38]. Aforementioned papers, however, discuss transfer of only ClO_4^- anions and they lack systematic study of the effect of ion hydrophobicity and ion concentration on the voltammetric peak potentials. These two effects are fundamental at droplet TPEs and can be used in chemical analysis for ion identification. The thermodynamic model for ion transfer by Scholz et al. [30] is based on the Nernst equation and assumes local equilibrium between the ion concentrations on either side of the liquid|liquid interface and the liquid junction potential. Whether this model can be applied to an inherently non-equilibrium system such as a microfluidic TPE still remains unanswered.

The aim of this work was to determine if the thermodynamic model of electrochemically driven ion transfer processes at droplet TPEs can be applied to microfluidic systems, despite that the latter operate under non-equilibrium conditions. We have compared two effects typically observed at droplet-modified electrodes: (1) the effect of counterion hydrophobicity on the peak potential and (2) effect of counterion concentration on the peak potential. Additionally, we have determined Gibbs energies of transfer for the investigated ions in the NOP-water biphasic system.

2. Experimental

2.1. Chemicals and materials

Decamethylferrocene (DMFc) (97%, ABCR), N-octyl-2-pyrrolidone (NOP) (98%, Santa Cruz Biotechnology), tetraheptylammonium tetraphenylborate ($THepA^+TPB^-$) (Selectophore, Fluka), tetrahexylammonium perchlorate ($THxA^+ClO_4^-$) (ABCR), tetraoctylammonium nitrate ($TOA^+NO_3^-$) (99%, Sigma-Aldrich), tetraoctylammonium bromide (TOA^+Br^-) (98%, Sigma Aldrich), tetraphenylarsonium chloride ($TPAs^+Cl^-$) (99%, Strem Chemicals), sodium tetraphenylborate (Na^+TPB^-) (Selectophore, Fluka), potassium tetrakis(4-chlorophenyl)borate (K^+TPBCl^-) (98%, Sigma-Aldrich) and inorganic salts of analytical grade: KPF_6 (98%, Sigma-Aldrich), $NaClO_4$ (>99%, Fluka), NaSCN (purum, Fluka), KNO_3 (99%, POCh), KBr (pure p.a., POCh), NaCl (>99.99%, Fluka), NaF (pure p.a., POCh) were used as received. Tetraphenylarsonium tetrakis(4-chlorophenyl)chloride ($TPAs^+TPBCl^-$) was synthesized by metathesis and purified by two recrystallizations in acetone. Poly(dimethylsiloxane) (PDMS) elastomer and curring agent (Sylgard 184, Dow Corning) were used as received. AZ ECI 3027 positive photoresist, SU-8 2100 negative photoresist were purchased from Microchemicals GmbH. Silicon wafers were purchased from Topsil Semiconductor Materials S.A. Water was filtered and demineralized with ELIX system (Milipore).

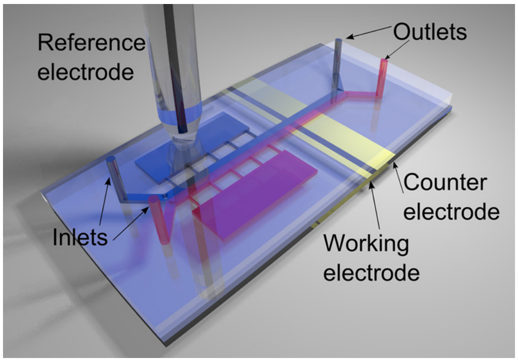

Fig. 1. Scheme of a microfluidic chip used for studying ion transfer across NOP|W interface under multiphase flow conditions.

2.2. Fabrication of microfluidic system

The microfluidic system with integrated gold band electrodes was prepared by soft lithography and PDMS micromoulding procedures described in our previous work [38]. The system consists of two inlets, two outlets, a central channel (500 μm wide and 200 μm height) and two side-reservoirs, each connected to the central channel by four capillary channels (2 mm long and 50 μm wide) (Fig. 1). In the aqueous-side reservoir an Ag|AgCl|3 M KCl reference electrode was placed. The second reservoir on the organic-side was not used in this work, however it can be used for the second reference electrode to measure the liquid junction potential [39].

2.3. Electrochemical measurements

Cyclic voltammetry (CV) and square-wave voltammetry (SWV) were performed with an Autolab potentiostat (Metrohm Autolab B.V., Netherlands). Parameters for SWV were: frequency 8 Hz, step potential 1 mV, amplitude 50 mV. All measurements were performed with a silver-silver chloride electrode (Ag|AgCl|3 M KCl) as a reference electrode. All measurements were made at room temperature (23 ± 2 °C).

Microfluidic systems. Working and counter gold band electrodes were located at the bottom of the main channel perpendicular to the flow direction. The Ag|AgCl|3 M KCl electrode was placed in the aqueous-side reservoir. During the electrochemical measurements, the flow rate of the aqueous phase ($V_{f,aq}$) was set 8 times higher than the flow rate of the organic phase ($V_{f,org}$) to keep the widths of the parallel aqueous and organic phases streams equal [35] with the exception of the measurements of its dependence on peak potentials the flow rates were kept constant at $V_{f,aq} = 40\ \mu L\ min^{-1}$ and $V_{f,org} = 5\ \mu L\ min^{-1}$. To control the flow of the aqueous and organic phase, two syringe pumps (Harvard Apparatus, Pump 11 elite) were used. The syringes were connected to the microfluidic system via polyethylene tubing.

Droplet-modified electrodes. A glassy carbon (GC) electrode with an active area of 0.031 cm^2, and platinum wire were used as working and counter electrodes, respectively. First, the GC electrode was polished with 1, 0.3, and 0.05 μm Al_2O_3 (Buehler) slurry and sonicated in demineralized water. Next, a microliter droplet of the