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Microfluidic chip for electrochemically-modulated liquid|liquid extraction of ions

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Abstract

A microfluidic device with integrated electrodes for the electrochemically-modulated extraction of ions across immiscible aqueous–organic liquid–liquid interfaces is presented. Using a Y-shaped microfluidic channel with *in situ* electrodes and co-flowing aqueous and organic immiscible electrolyte solutions, the manipulation of the applied interfacial potential enabled the extraction of ions from the aqueous phase into the organic phase. Data for the extraction of tetraethylammonium cations from aqueous electrolyte into 1,2-dichloroethane electrolyte are presented. The device demonstrates the benefits of combination of microfluidics and liquid–liquid electrochemistry.

Keywords: Microfluidics; ITIES; Laminar flow; Ion transfer; Extraction

1. Introduction

Liquid extraction techniques are usually employed for sample pre-treatment to remove interfering substances, preconcentrate and/or increase the sensitivity of analytical methods. Liquid|liquid extraction (LLE) is widely used in preparative and analytical chemistry despite difficulties such as non-trivial automation of the process, slow inter-phase transport and phase separation efficiencies. However, microfluidics offers new opportunities for improvements based on the enhanced surface area-to-volume ratio, faster diffusion and thus more efficient extractions and phase separations [1]. In microfluidic devices, Reynolds numbers are such that laminar flow of adjacent solution phases occurs and separation and molecular transport [2] take place without convective mixing. In such conditions, small molecules can redistribute between adjacent fluid layers [3,4].

Extraction processes and liquid–liquid partitioning within microfluidics devices are well known [4–13]. Multiphase flows offer important advantages in microfluidic systems [14] such as the ability to separate compounds from one another or to prepare new materials on a small scale. These multiphase devices offer many possible applications, serving as a sample preparation or preliminary treatment step, or even as a means of characterising substances. For example, the ability to miniaturise and automate octanol–water partition coefficient measurements within microfluidic systems [15] is attractive as it can speed-up and enable parallelisation of assays together with minimisation of reagent consumption and waste production. Microfluidic LLE has been investigated for various applications in extractions [1,4–13,16–18] and for the separation of amino acids [19] or proteins [20,21].

These advances rely on the natural propensity for a solute to diffuse from one phase to another and hence external control and selectivity in the extraction process is absent. However, ionic solutes can be intentionally transferred from an aqueous electrolyte to an organic electrolyte (or vice versa) by imposition of suitable applied potentials,

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referred to as electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) [22,23]. The potential necessary to promote the transfer of an ion across the ITIES depends on the ion's Gibbs energy of transfer, which is the difference in solvation energies of the ion in the two solvents. By imposing applied potentials that make the aqueous phase more positive than the organic phase, a cation can be induced to transfer from the aqueous into the organic phase. However because different species will have different Gibbs energies of transfer, these ions can be induced to transfer at different potentials in a voltammetric experiment. We recently proposed the use of electrochemically-modulated liquid–liquid extraction of ions [24,25] as a means for externally-controlled extractions suitable for sample preparation activities, because electrochemistry at the ITIES had previously only been suggested as a detection method. The different transfer potentials of ions mean that the applied potential can be customized for the extraction of a particular analyte ion in the presence of other ions in the sample, hence imparting selectivity to the extraction or separation process [24,25]. Although hydrodynamic liquid–liquid electrochemical processes have been reported [26–28] and a device suited to liquid–liquid electrochemical microfluidics was described [29], no ion transfer reactions across the microfluidic ITIES have been reported. However, a recent communication described a microfluidic three-phase (liquid–liquid–solid) electrochemical system [30]. Furthermore, Yager [31] proposed the use of liquid-junction potentials provided by transport of ions across phase boundaries for transverse electrophoretic separations, while Girault [32] investigated that process experimentally and theoretically. The disadvantage of liquid-junction potentials is that they can only be changed by changing the solution composition. No practical demonstration of microfabricated microfluidic chip-based liquid–liquid ion transfer electrochemistry has been reported.

In this communication, we present preliminary data for the miniaturisation of electrochemically-modulated liquid–liquid extractions [24,25] within a microfluidic channel in which the aqueous and organic phase electrolyte solutions undergo parallel laminar flow, harnessing the benefits of microfluidics [1,3]. We demonstrate the *in situ* electrochemical transfer of ions across the microfluidic hydrodynamic ITIES. The *in situ* electrodes enable the direct imposition of applied potentials together with the *in situ* measurement of the results of ion movement across the phase boundary (i.e. the current is a direct *in situ* measurement of the process).

2. Experimental

The microfluidic devices were fabricated on silicon substrates, using standard photolithographic, deposition and etching techniques. Fig. 1 shows a general schematic of the devices. These consisted of a silicon substrate with patterned platinum electrodes (150 nm thick) onto which the microchannels were then prepared using SU8 resist (180 μm high). The platinum electrodes protruded 75 μm into the central channel from the SU8 at the base of the channel walls, so that the separation between opposite electrodes was 350 μm and they are close to the aqueous/organic interface. Hence, each fluid phase possessed one inserted electrode, serving as pseudo-reference and counter electrode, so that electrochemistry at the ITIES formed within the channel can be applied. The electrodes were 1.5 cm in length and located in the middle of the central extraction channel. The channel geometry was Y-shaped,

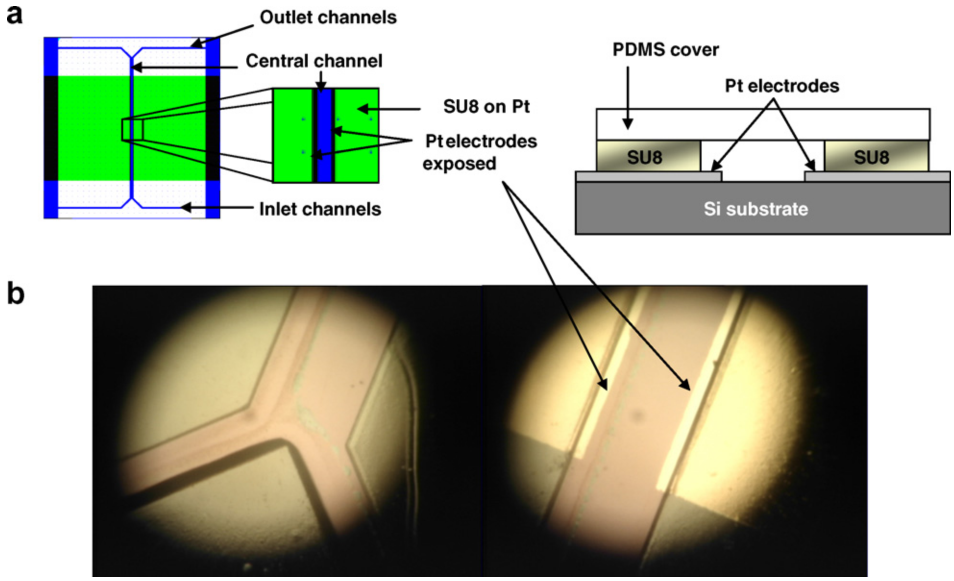

Fig. 1. (a) Schematic diagram of the liquid–liquid microfluidic electrochemical device: left: top view sketch showing channel design and electrode locations; right: cross-section of the main channel showing location of the electrodes. (b) Photographs of (left) the microchannel Y-junction where the inlet channels meet the main channel and (right) the electrodes at the base of the main channel, on each side.