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Ion transfer kinetics at the micro-interface between two immiscible electrolyte solutions investigated by electrochemical impedance spectroscopy and steady-state voltammetry

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ABSTRACT

The kinetics of tetraethylammonium (TEA^+) ion transfer across the water/1,2-dichloroethane interface was studied using electrochemical impedance spectroscopy and steady-state voltammetry. The liquid/liquid interface was supported at the tip of a microcapillary. A novel capillary design methodology has advantageously allowed the use of the same microcapillary in a number of different experiments. It is herein shown that the geometry of the microcapillary tip region is of critical importance in order to obtain reliable kinetic data. Both steady-state voltammetry and electrochemical impedance spectroscopy yielded approximately the same apparent standard rate constant of 0.2 cm s^{-1} for TEA^+ transfer across the water/1,2-dichloroethane.

1. Introduction

Experimental platforms provided by a liquid–liquid interface, such as that formed between two immiscible electrolyte solutions (ITIES) for example, enable the study of a wide range of important interfacial processes. Research centred on ITIES-based systems has dealt with both academically and industrially relevant interfacial processes such as interfacial charge-transfer, complexation, ion-pairing and electrocatalysis (for comprehensive surveys see references [1–7]). At the heart of most of these interfacial processes is the actual charge-transfer process itself. Interfacial charge-transfer reactions are additionally of fundamental interest as these reactions play a pivotal role in many important and interesting physiochemical and biological processes [7].

Electrochemical cells with planar liquid–liquid interfaces, have been in common use for a long time. A flat interface and geometric configuration of these four electrode electrochemical cells are of critical importance for ensuring homogeneous polarization of the interface [8]. Recent research has focused on the use of micro/nanoscopic liquid–liquid interfaces to study the kinetics of the interfacial charge-transfer process [6]. Extensive use of micro/nanoscopic liquid–liquid interfaces has been largely driven by the hope that small-area liquid–liquid interfaces may provide better insight into the mechanisms which govern the kinetics associated with interfacial charge-transfer [9].

An extremely important parameter with respect to the kinetics of interfacial charge-transfer is the charge-transfer resistance (R_{ct}). The charge transfer resistance does not however solely influence the electrical behaviour of the electrochemical cell. In fact, the extent of the cell solution resistance (R_s), mass transport impedances, interfacial double layer capacitance (C_{dl}) and stray capacitance (associated with commonly-used electrochemical experimental arrangements [5]) can often render the determination of R_{ct} unreliable [9].

A common electrochemical methodology used to measure interfacial rate constants is nanopipette voltammetry conducted under steady-state conditions [6]. By decreasing the surface area of the liquid–liquid interface toward the nanoscale, the ratio of the charge-transfer resistance to both mass transfer resistance and solution resistance increases, thereby enabling a presumably more accurate determination of the charge-transfer resistance. Additionally, the steady-state technique is also known to be very useful in nullifying the effects of any unwanted capacitive current. The use of nanopipettes in conjunction with the steady-state technique, has however produced unexpected and surprising results, in terms of the magnitude of values thus obtained for the rate of ion transfer across the ITIES [10].

The simple ion transfer of tetraethylammonium (TEA^+) across the water (w)/organic solvent (o) interface has been widely used as a convenient exemplar model kinetic system [6,9,12]. Its wide

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usage stems from the fact that the transfer of TEA^+ from water to oil has a small standard Gibbs energy of ion transfer [13,14], this allows one to neglect electric field effects near the ITIES, especially those which arise from double layer effects.

The most recent estimates of the rate of TEA^+ ion-transfer at nanoscopic interfaces formed at the tips of pulled glass capillaries are in the order of 100 cm/s [10] which contrasts sharply with those values ($\sim\leqslant 1$ cm s^{-1}) obtained at macroscopic ITIES (area 0.1–1 cm^2) [13]. In a recent analysis of previously published kinetic data [15], it was concluded that the extremely high rate constant of ca. 100 cm s^{-1} [10] was probably overestimated due to an inadequate expression that was used to describe the mass transfer coefficient. It was further suggested that a corrected value could be in the order of approximately 10 times smaller.

The kinetic analysis of nanopipette voltammograms may become complicated by electrostatic effects associated with the negatively charged (glass) capillary walls [11]. These effects could influence ion transport adjacent to the wall and also across the liquid–liquid interface (directly located at the nanopipette orifice) [16,17]. Furthermore, it has been shown [17,18] that ion transport in charged conical nanopores can give rise to ion current rectification effects. Another source of concern, is associated with the electric field within the space charge region at the liquid–liquid interface [16] when the Debye length, characterizing the thickness of the space charge region ($\sim$3 nm for a 0.01 M uni–univalent electrolyte) is comparable to the thickness of the diffuse layer, i.e., to the inner radius of the nanopipette. Qualitatively, this effect leads to an acceleration of the transfer of a cation from the positively charged aqueous phase to the negatively charged organic solvent phase. Model calculations [19] suggest that the effect could be significant for the nanoscopic ITIES with the radii smaller than 100 nm.

We have previously used electrochemical impedance spectroscopy (EIS) under equilibrium conditions in conjunction with microscopic interfaces and have obtained rate constants in the order of >0.2 cm s^{-1} [9]. In contrast to nanopipette voltammetry conducted under steady-state conditions, these values are indeed similar to those values obtained at the macroscopic ITIES. Using fluctuation analysis (FA) we have shown that local interfacial micro-convections are likely to be induced when conducting EIS at frequencies below 10 Hz [20]. These induced micro-convections could disturb the ion concentration profiles at a liquid–liquid boundary when low-frequency EIS or steady-state nanopipette voltammetry techniques are used.

In this paper, we compare kinetic data obtained for the transfer of TEA^+ across the water/1,2-DCE interface from electrochemical impedance spectroscopy and steady-state voltammetry. For this purpose we use a novel capillary design methodology, which allows a number of different experiments to be conducted using the same capillary. In this way, we are able to show that kinetic data obtained using steady state voltammetry is similar to kinetic data obtained using electrochemical impedance spectroscopy. Experimental errors which hinder the gathering of accurate kinetic data are discussed.

2. Experimental

LiCl, tetraethylammonium chloride (TEACl), tetrabutylammonium chloride (TBACl), tetrabutylammonium tetraphenylborate (TBATPB) were reagent grade and were supplied by Fluka AG. Chemicals were used as received. Tetraethylammonium dicarbollylcobaltate(III) (TEADCC) was prepared at the Institute of Inorganic Chemistry ASCR, v.v.i.

Highly purified and deionized water (conductance: <0.1 μS cm^{-1}, GORO system, Czech Republic) was used to prepare aqueous solutions. 1,2-dichloroethane (1,2-DCE, 99%, Penta) was used for all organic solutions.

Capillaries used throughout this paper were manufactured and filled with electrolyte solution in a manner analogous to that previously reported [21]. The geometry of a typical capillary is shown in Fig. 1. Capillaries were silanised using a previously published silanization protocol [15] with chlorotrimethylsilane (Sigma Aldrich).

Throughout this paper we make use of three different experimental arrangements. The first of which is termed the 'single phase experiment'. This experimental arrangement involves the same aqueous phase/electrolyte both inside and outside the silanised capillary. It does not involve a liquid/liquid interface. A typical electrochemical cell for this arrangement is:

$$\mathrm{Ag/AgCl}/x\ \mathrm{mMLiCl} + y\ \mathrm{mMTEACl\ (w)/AgCl/Ag} \quad (1)$$

The second type of experiment is termed the 'EIS experiment'. The liquid/liquid interface is supported at the tip of a silanised microcapillary using a cell with an open circuit potential of 0 V:

$$\begin{aligned}&\mathrm{Ag/AgCl}/x\ \mathrm{mMLiCl} + y\ \mathrm{mMTEACl\ (w)}/x\ \mathrm{mMTBATPB}\\&\quad + y\ \mathrm{mMTEADCC\ (o)}/x\ \mathrm{mMLiCl} + y\ \mathrm{mMTEACl\ (w)/AgCl/Ag}\end{aligned} \quad (2)$$

The third type of experiment is termed the 'cyclic voltammetric experiment' with the liquid–liquid interface supported at the tip of a silanised glass microcapillary. A typical electrochemical cell for this micro-ITIES may or may not contain TEACl, and is as follows:

$$\begin{aligned}&\mathrm{Ag/AgCl/10\ mMLiCl}\\&\quad + 1.6\ \mathrm{mMTEACl\ (w)/10\ mMTBATPB\ (o)/10\ mMTBACl\ (w)/AgCl/Ag}\end{aligned} \quad (3)$$

All electrochemical experiments were conducted using a CHI 660c potentiostat (CHI Instruments). Impedance measurements were performed in a frequency range from 10 Hz to 10 kHz with a 20 mV peak to peak amplitude perturbation. Impedance spectra were fitted using the equivalent circuit shown in Fig. 2 and software installed on the CHI 660c potentiostat. Further analysis of the impedance spectra using LEVM/LEVMW ver.8.06 software was also used on occasion.

All measurements were carried out at ambient temperature, i.e., 295 ± 2 K.

3. Results and discussion

3.1. EIS

The EIS technique [9] makes use of an electrochemical cell in equilibrium. A small electrical perturbation is applied to the cell,

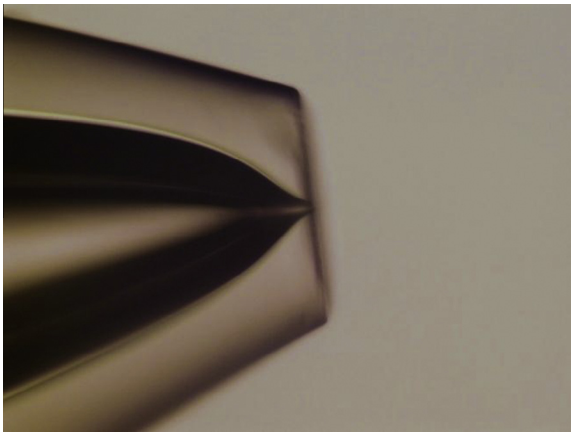

Fig. 1. Typical capillary design used in experiments. The capillary orifice radius is 4 μm, half-cone angle is 10.5 degrees.