



Ion transfer at polarised liquid-liquid interfaces modified with adsorbed silica nanoparticles



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ABSTRACT

The interface between two immiscible electrolyte solutions (ITIES) can act as a scaffold for the assembly of nanometer-sized objects. Here we followed the adsorption of silica nanoparticles of 12 nm diameter at the ITIES by AC voltammetry and their interactions with methylene blue (MB^+), selected as a model ion, by cyclic voltammetry and UV–vis absorption spectroscopy. We determined the association constant, K_{ads}^{aq} , of adsorption of MB^+ onto silica nanoparticles to be $1.66 \cdot 10^5$, which indicated a strong affinity between them. This strong affinity shifted the Gibbs free energy of transfer by -8.9 kJ mol^{-1} . This is in contrast with the other two ions investigated (Eosin B and tetraethylammonium), which demonstrated low affinity for the silica nanoparticles. By combining the ability of silica to adsorb onto the ITIES and their affinity for MB^+ , we were able to accumulate MB^+ at the ITIES.

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1. Introduction

The interface formed between two immiscible electrolyte solutions (ITIES) is a highly reproducible, defect-free surface that allows the assembly of a large variety of nanoscale objects [1–4]. The adsorption of nano-objects at a liquid-liquid interface is governed by their dimensions, the organic-aqueous interfacial tension and the wettability of the material [2,5–8]. The ITIES allows the application of an external electric field that can drive the adsorption of nanoparticles (Au or TiO_2) to the interface [9–11]. Carbon nano-materials (e.g. carbon nanotubes, graphene and graphite flakes) [12–15] and gold nanoparticles [16,17] adsorbed at the ITIES improve electron transfer kinetics between electron donors and acceptors distributed on either sides of the interface [14–17]. The nano-objects assembled at the interface act as conductive rafts floating at the interface catalysing electron transfer through Fermi level equilibration [18,19]. Gold nanoparticles have also been injected onto the interface between a mixture of heptane and 1,2-dichloroethane and water to form a self-assembled monolayer, which exhibits reflectance and electrical conductance, opening the way to the development of electrovariable optical materials [20].

Despite the abundant literature on silica nanoparticles [7,21–25], their assembly at the ITIES has not been investigated yet. Nevertheless, silica sphere structures have been self-assembled at non-polarised liquid-liquid interfaces to fabricate 2 or 3D ordered structures with potential applications in optical, magnetic and electronic devices as photonic band gap materials [26]. Li et al. modified the surfaces of silica spheres and then self-assembled them at the liquid-liquid interface in order to fabricate 2D/3D film structures [26]. The ability to generate low-dimensional nanostructures is by far the most popular application of self-assembled silica nanoparticles at non-polarised liquid-liquid interfaces. The film obtained at the interface after spontaneous adsorption of the silica nanoparticles has low resistance to lateral motion and so is transferrable, allowing it to be used for other applications [27]. The growing interest for the use of silica-based materials at the liquid-liquid interface is also due to their favourable adsorption kinetics and selectivity [28], which could be harnessed to the development of new sensing methods [29,30]. ITIES was modified by the electrogeneration of mesoporous silica deposits [31–35], which were the result of an electrochemically driven ion transfer followed by interfacial precipitation. Mesoporous silica was generated at the ITIES by the transfer of a cationic surfactant (e.g. trimethylhexadecylammonium) from the organic phase to the aqueous phase containing hydrolysed tetra(alkoxy)silanes, catalysing the condensation reactions of the sol-gel process.

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Micro-ITIES arrays were also modified with mesoporous silica channels prepared ex-situ by a Stöber-like method [36]. The vertically aligned channels obtained have demonstrated their potential for analytical applications [37–40]. We investigated here the adsorption of silica nanoparticles onto the ITIES and their impact on the electrochemical transfer behaviour of ions (e.g. methylene blue, eosin B and tetraethylammonium) in the view of developing new analytical methods. Since silica nanoparticles themselves do not have any electrochemical signal at the ITIES they can serve as an aid to enhance the selectivity and preconcentration of target ionic species at the interface and thus their transfer across the ITIES. This ability to detect ionic species is of major benefit in both environmental monitoring and clinical diagnosis. The sensing of synthetic organic molecules, such as drug molecules and pollutants, using silica nanoparticles adsorbed at the ITIES to improve sensitivity is of significant interest.

2. Experimental section

2.1. Chemicals & reagents

The high density organic phase electrolyte was 1,2-dichloroethane (1,2-DCE, $\geq 99\%$ Sigma-Aldrich) containing 10 mM Bis (triphenylphosphoranyldiene) ammonium tetrakis (4-chlorophenylborate) (BTTPA⁺ TPBCl⁻). The organic salt was prepared by metathesis of Bis (triphenylphosphoranyldiene) ammonium chloride (BTTPA⁺ Cl⁻, 97% Aldrich) and Potassium tetrakis (4-chlorophenylborate) (K⁺ TPBCl⁻, $\geq 98\%$ Fluka) [31]. Lithium Chloride (LiCl, $\geq 99\%$ Aldrich) was used as the aqueous phase electrolyte. Solutions of the interfacial active ions: Tetraethylammonium chloride (TEA⁺ Cl⁻, $\geq 99\%$ Fluka), Methylene Blue (>82% Fluka) and Eosin B (>85% Sigma-Aldrich), were prepared in the aqueous phase electrolyte. The Ludox[®] HS-40 colloidal silica ($\varnothing_{mean} = 12$ nm, $10.6 < \varnothing < 13.7$ nm) was purchased from Aldrich. Ferric chloride hexahydrate (FeCl₃·6H₂O, $\geq 99\%$ Fluka) was used to prepare silver/silver chloride reference electrodes.

2.2. Experimental methods

The custom-made electrochemical cell ($A_{interface} = 1.13$ cm²) consisted of 2 sets of platinum mesh and silver/silver chloride wires as counter and reference electrodes respectively for both aqueous and organic phases. Different electrochemical cells were used and their compositions were as follows:

- Electrochemical cell 1

Ag_(s) | AgCl_(s) | 10 mM LiCl_(aq) x mM interfacial active ion_(aq) + X g L⁻¹ silica nanoparticles || 10 mM BTTPA⁺TPBCl⁻_(org) in 1,2-DCE | Saturated BTTPA⁺Cl⁻ in 10 mM LiCl in H₂O | AgCl_(s) | Ag_(s);

- Electrochemical cell 2

Ag_(s) | AgCl_(s) | 100 mM LiCl_(aq)+X g L⁻¹ silica nanoparticles || 10 mM BTTPA⁺TPBCl⁻_(org) in 1,2-DCE | Saturated BTTPA⁺Cl⁻ in 10 mM LiCl in H₂O | AgCl_(s) | Ag_(s);

- Electrochemical cell 3

Ag_(s) | AgCl_(s) | 10 mM HCl_(aq) + X g L⁻¹ silica nanoparticles || 10 mM BTTPA⁺TPBCl⁻_(org) in 1,2-DCE | Saturated BTTPA⁺Cl⁻ in 10 mM LiCl in H₂O | AgCl_(s) | Ag_(s);

- Electrochemical cell 4

Ag_(s) | AgCl_(s) | Saturated BTTPA⁺Cl⁻ in 10 mM LiCl in H₂O | 10 mM BTTPA⁺TPBCl⁻_(org) in 40:60 1,2-DCE:5-nonanone (v/v) || 10 mM LiCl_(aq) x mM interfacial active ion_(aq)+X g L⁻¹ silica nanoparticles | AgCl_(s) | Ag_(s).

Two electrochemical techniques were used during these experiments – Alternating Current (AC) Voltammetry and Cyclic Voltammetry (CV). Cyclic voltammetry experiments were run with an Autolab 302 N potentiostat using Nova 1.10.1.9 software by Metrohm Autolab B.V. The formal transfer potential of TEA⁺, $\Delta_o^w \phi_{TEA^+}^o = 0.049$ V [41], was used to calibrate the potential window. TEA⁺ was added to the aqueous phase of the electrochemical cell at the end of a series of experiments for potential calibration purposes. For CV experiments, the transfers of Li⁺ and Cl⁻ from the aqueous phase to the DCE phase establish the positive and negative limits of the potential window, respectively. In the presence of SiO₂, the potential was calibrated using the limits of the potential window as previous studies have shown that the transfer of both Li⁺ and Cl⁻ is not hindered by the presence of electrogenerated silica [33]. Scans were run at a scan rate of 5 mVs⁻¹. AC voltammetry experiments were run using GPES software with an Autolab PGSTAT-12. Parameters for the AC experiments were as follows - modulation time: 0.33 s, interval time: 0.73 s, frequency: 6 Hz, step potential: 5 mV, amplitude: 5 mV RMS. The potential region was scanned at phase angles of 0° and 90°. In this frequency range, the impedance response of the cell is determined by a single RC component associated with the uncompensated resistance and the double-layer capacitance [10,42].

UV/Vis absorption spectroscopy experiments were carried out using an Agilent Technologies Cary 60 UV–Vis spectrometer. Solutions analysed were prepared in 10 mM LiCl and poured in standard plastic cuvettes with a path length of 1 cm. For the determination of the association constant and the total number of adsorption sites by UV–vis absorption spectroscopy, solutions of 50 μ M of MB⁺ in 10 mM LiCl with varying concentrations of SiO₂ nanoparticles (final silica nanoparticle concentrations were between 0.040 and 0.867 g L⁻¹, total volume was 10 mL) were poured in a stirred ultrafiltration cell (25 mm diameter, Amicon Model 8010, Millipore, Carrigtwohill, Ireland) equipped with a regenerated cellulose membrane (PLGC, 10 kDa, Millipore). The filtrate was collected and analysed by UV–vis absorption spectroscopy. Pre-concentration experiments were prepared with 200 mL of a 25 μ M MB⁺ solution containing 0.05 g L⁻¹ of SiO₂ nanoparticles. The solutions were mixed for 5 min and then centrifuged at 10,000 rpm for 15 min. The supernatant was removed and 3 mL of a 10 mM LiCl solution was added to the nanoparticle-MB⁺ precipitate, which is then used as the aqueous phase in the electrochemical cell.

3. Results and discussion

3.1. Silica nanoparticles adsorption at the ITIES

Previous studies on the behaviour of nanoparticles at the liquid-liquid interface have shown that their adsorption is the result of the presence of a promoter or a modifier that weakens the electrostatic repulsion between the nanoparticles in suspension and allows the assembly of nanoparticles at the interface [43]. An alternative to this chemically induced assembly is the application of an interfacial potential difference that causes the assembly [9]. The adsorption of silica nanoparticles was investigated here by both cyclic and AC voltammeteries at the ITIES (Fig. 1). After the addition of 0.5 g L⁻¹ silica nanoparticles to the aqueous phase, there was no significant changes to the CV, suggesting that no ion transfer is taking place in the potential window due the presence of the silica nanoparticles.

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