Contents lists available at ScienceDirect

Electrochemistry Communications

Electrochemical monitoring of the co-extraction of water with hydrated ions into an organic solvent

Vladimír Mareček

J. Heyrovský Institute of Physical Chemistry of the CAS, Dolejškova 2155/3, 182 23 Prague 8, Czech Republic

ARTICLE INFO

ABSTRACT

An electrochemical cell based on the interface between two immiscible electrolyte solutions (ITIES) was designed and used to study the co-extraction of water with hydrated chloride ions from the aqueous to the organic solvent phase. The interfacial potential was controlled by the distribution of a common tetralkylammonium (TAA^+) ion. Transfer of hydrated chloride ions is accompanied by the transfer of TAA^+, decreasing its concentration on the aqueous side of the interface. Changes in the TAA^+ concentration at the interface were monitored by measuring the open circuit potential (OCP). The proposed mechanism of TAACl transport involves a follow-up reaction with the co-extracted water molecules, leading to the formation of clusters of water containing TAACl in the organic phase.

1. Introduction

Co-extraction of water by hydrated anions has been studied by a range of methods, including spectroscopy, NMR and solubility measurements [1]. The amount of water co-extracted by halide anions into different solvents has always been found to decrease in the order $F^- > Cl^- > Br^- > I^-$ [1]. It has also been found that the hydration numbers of the halide anions increase with increasing concentration of the tetraalkylammonium salt in the organic phase, probably due to the formation of ion pairs and higher ion aggregates, especially in solvents with a low permittivity. Since the alkylammonium cations are anhydrous [2], their presence does not contribute to water extraction.

The structure of water in the organic phase has been studied using FTIR spectroscopy [3]. It has been found that water–anion clusters assume the same topology as water-only clusters. The stability of these molecular networks has been investigated theoretically [4]. However, only a few studies have reported data characterizing the ion solvation kinetics. It has been shown that the solvation dynamics of various lithium solvatomers in nitrobenzene obey first-order kinetics with the rate constant as low as $10^{-5}\,s^{-1}$ [5].

In the present paper, we introduce an electrochemical method that makes it possible to monitor the dynamics of the TAACl partition process at the interface between two immiscible electrolyte solutions. This process involves the co-extraction of water molecules with the hydrated chloride ions and the formation of water clusters in the organic solvent phase. The ability to monitor the process from the very beginning of interface formation allowed us to obtain important kinetic data.

2. Experimental

2.1. Chemicals and cell

Tetrabutylammonium chloride (TBACl), tetrabutylammonium tetraphenylborate (TBATPB) and tetrapentylammonium chloride (TPeACl) were supplied by Fluka AG and used as received (reagent grade). Tetrapentylammonium tetraphenylborate (TPeATPB) was prepared by metathesis. Electrolyte solutions were prepared using deionized water ($< 0.1\,\mu S\,m^{-1}$, GORO system, Czech Republic) and 1,2-dichloroethane (1,2-DCE, 99%, Penta).

A two-electrode cell comprising a liquid/liquid interface supported at the tip of an L-shaped glass capillary with an orifice diameter of 1.5 mm was used throughout:

$$Ag/AgCl/(10 - x)\,mM\,NaCl\ + x\,mM\,TAACl(w)//10\,mM\,TAATPB(o)$$

$$/10\,mM\,TAACl(w')/AgCl/Ag \tag{1}$$
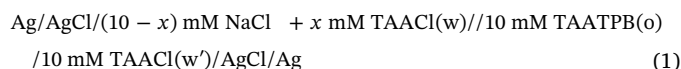
where $x = 1$ or 10, and TAA is TBA or TPeA.

The cell potential difference can be written as

$$E = (RT/F)\ln c^w_{TAA+}/c^o_{TAA+} \tag{2}$$

where c^w_{TAA+} and c^o_{TAA+} represent the concentrations of TAA^+ on the aqueous and the organic side of the interface, respectively.

The capillary was filled with the aqueous phase (w) and immersed in the organic phase (o) (volume < 2 ml). A small air bubble was left in the capillary tip to prevent contact between the phases before the first OCP measurement. As soon as the first OCP measurement started the air

---
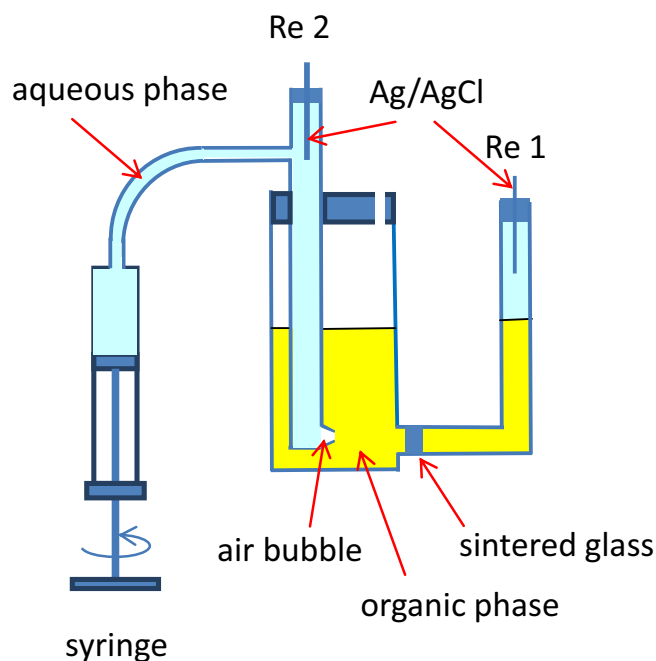
Fig. 1. Schematic diagram of the electrolytic cell.
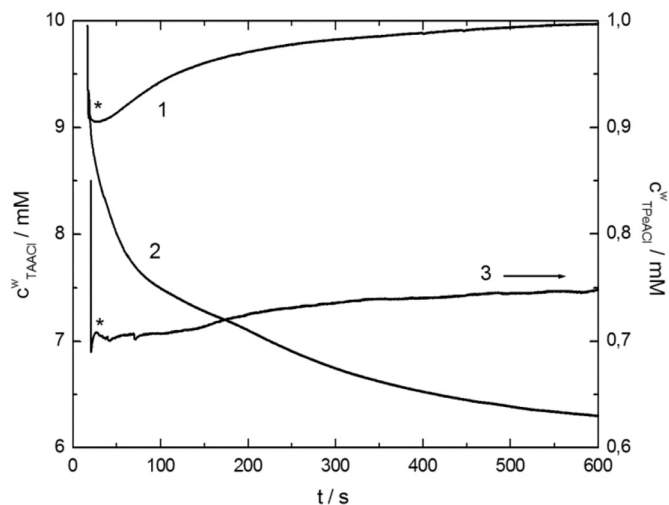

Fig. 2. Initial OCP records of cell (1) after creating the water/organic interface. Potential scale is converted to concentration (see the text). (Experiments 1 and 2) $x = 10$ mM; (Experiment 1) TAACl = TBACl; (Experiment 2) TAACl = TPeACl; (Experiment 3) $x = 1$ mM; TAACl = TPeACl. (*) initial concentration change.

bubble was ejected by a syringe connected to the capillary. This procedure enabled the OCP measurement to start at defined initial conditions. A syringe was also used to refresh the interface by renewing the aqueous phase. In all experiments, the organic phase was equilibrated with pure water before preparing the cell. A schematic diagram of the cell is shown in Fig. 1.

2.2. Apparatus

A homemade low-noise–high-impedance differential input preamplifier was constructed using an operational amplifier INA116 (Texas Instruments). The battery-operated preamplifier (amplification 5.22) and the cell were placed within a grounded Faraday cage. The preamplifier output was connected to the Solartron SI 1287 Electrochemical Interface (England) to record the cell OCP. All measurements were conducted at a temperature of 295 ± 2 K.

3. Results and discussion

The electrochemical cell (1) with three different compositions is used to study the effect of interfacial potential on the dynamics of water co-extraction by chloride ions into the organic phase. In the first experiment, the working interface is polarized by an equal concentration of TBA$^+$ ion in both phases. In the other two experiments the interface was polarized by the distribution of the TPeA$^+$ ion, with a different concentration of TPeA$^+$ in the aqueous phase (10 or 1 mM). The induced potential difference changes the partition of Cl$^-$ between water and organic phase, resulting in the following concentrations of Cl$^-$ in 1,2-DCE: 0.46 μM for TBA$^+$, 8.8 μM for 1 mM TPeA$^+$ and 88 μM for 10 mM TPeA$^+$ [6]. The transfer of Cl$^-$ from the aqueous to the organic phase is accompanied by TAA$^+$ to maintain electroneutrality. Thus it can be assumed that the observed potential changes correspond to changes in the concentration of TAA$^+$ on the aqueous side of the interface.

Initial OCP(t) records for all three compositions of the cell are shown in Fig. 2. The interfacial potential is converted to concentration

(2) of c_{TAA+}^w, keeping c_{TAA+}^o constant. The OCP recording started at a time when both phases were separated by an air bubble inside the tip of the capillary. The bubble was then ejected by a syringe connected to the capillary (Fig. 1) and the solutions came into contact. This procedure made it possible to record the interfacial potential from the first contact of the two electrolytes. This moment can be seen in Fig. 2 as an abrupt concentration change (*) at the beginning of the curves. This concentration change depends on electrolyte concentration: for $c^w = 10$ mM the change is ~0.8 mM; for $c^w = 1$ mM the change is ~0.3 mM. The significant difference in the shapes of curves 1 and 2 demonstrates the effect of induced potential on chloride concentration in the organic phase. The slow concentration increase of TBA$^+$ after its initial drop to ~9 mM (see curve 1) indicates that the chloride transfer (accompanied by TBA$^+$) to the organic phase is rather slow and can be compensated by diffusion of TBACl from the bulk of the aqueous phase. It should be pointed out that diffusion of TBACl without transfer to the organic phase would result in a faster concentration increase. Quite different is the OCP record in the presence of 10 mM TPeA$^+$ (curve 2 in Fig. 2). After the initial concentration drop to ~9.2 mM, the concentration continues to decrease and in 600 s reaches 6.2 mM of TPeACl on the aqueous side of the interface. This clearly demonstrates enhancement of the TPeACl transport to the organic phase, which cannot be compensated by its diffusion from the bulk of the aqueous phase. Moreover, the decrease in concentration of TPeACl on the aqueous side of the interface considerably exceeds the decrease expected due to diffusion of TPeACl (88 μM) in the organic phase from the interface to the bulk. This indicates that the TPeACl transferred to the organic phase participates in a follow-up reaction, decreasing its concentration in the organic phase and thus enhancing its transport from the aqueous phase. A similar effect is observed when the concentration of TPeACl in the aqueous phase is ten times lower (curve 3 in Fig. 2). In this case, the interfacial potential is 60 mV higher and hence a lower concentration of chloride ions in the organic phase decelerates the transfer of TPeACl to the organic phase. This transfer is compensated by diffusion of TPeACl from the bulk aqueous phase, keeping its concentration on the aqueous side of the interface almost constant. Even in this case the diffusion flux of TPeACl in the aqueous phase should exceed that in the organic phase due to the very low concentration of TPeACl (8.8 μM) on the organic side of the interface. However, the increase in TPeACl concentration on