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Transfer of ionic liquids across the water/1,2-dichloroethane interface

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ABSTRACT

A fundamental electrochemical study of several highly diluted ionic liquids (ILs) at the interface between two immiscible electrolyte solutions (ITIES) is reported to evaluate the electrochemical and the solvation properties of [BMIM]Cl, [BMIM]BF₄, [BMIM]OTf, [EMIM]Br and [AMIM]Cl. The interface is formed between a hydrophilic electrolyte dissolved in water and a hydrophobic electrolyte dissolved in an organic solvent, here 1,2-dichloroethane (DCE). The transfer of the highly diluted ionic species from the water phase into the organic phase occurs when an electrical potential difference is applied across the interface. Standard Gibbs energy of transfer, the relative hydrophilicity/hydrophobicity and transfer coefficients across the interface of the selected ILs are determined by cyclic voltammetry at large ITIES.

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1. Introduction

Only a few fundamental electrochemical studies of ionic liquids (ILs) at the interface between two immiscible electrolyte solutions (ITIES) have been reported to evaluate the electrochemical and solvation properties of typical ionic liquids [1], although the electrochemistry at the ITIES is well known in the literature [2–5]. An interface is formed between a hydrophilic electrolyte dissolved in water and a hydrophobic electrolyte dissolved in an organic solvent, for example 1,2-dichloroethane (DCE). The transfer of the highly diluted ionic species from the water phase into the organic phase occurs when an electrical potential difference is applied across the interface. The resulting current flow is caused by the transfer of the ions across the interface.

Therefore, an ideal polarizable interface over a wide applied potential is needed. The polarization of an ITIES depends on the electrolyte ions in the water or organic phase. The potential window of the ideal polarizable interface, an area with negligible current flow, is a region between the transfers of the electrolyte ions across the interface. Hence, the supporting electrolytes should possess high Gibbs transfer energies. Moreover, they should dissolve sufficiently only in the water or in the organic phase to achieve high conductivity. They have to be strong hydrophilic or hydrophobic, respectively. Outside the potential window the electrolyte ions begin to move into the opposite phase resulting into increasing background currents: as the applied potential is made more positive $\varphi^w > \varphi^o$, a hydrophilic cation may transfer from the aqueous phase to the organic phase or a lipophilic anion may transfer in the opposite direction depending on their respective Gibbs energies of

transfer. The negative background current is determined by the hydrophilic anion and the lipophilic cation transfer.

The properties of an ion transfer across an ITIES are analogous to an electron transfer reaction at an interface between a metallic electrode and an electrolyte solution and can be characterized by the following parameters:

- a shift of the peak potential of the forward and backward scan (E_p^{fwd} and E_p^{bwd}) depending on the scan rate v ;
- the difference of the peak potentials of the forward and backward scan (E_p^{fwd} and E_p^{bwd});
- the quotient of the forward peak current and the square root of the scan rate $\frac{i_p^{fwd}}{\sqrt{v}}$;
- the ratio of the forward and backward peak currents $\frac{i_p^{bwd}}{i_p^{fwd}}$.

For a diffusion controlled uninhibited and an inhibited ion transfer different parameters are valid, which are summarized in Table 1.

For a reversible ion transfer reaction, the standard ion transfer potential $\Delta_o^w \varphi_i^o$ of an ion i , which can partition between the organic (o) and the aqueous (w) phase, is described by the following equation derived by Nernst formalism

$$\Delta_o^w \varphi = \Delta_o^w \varphi_i^o + \frac{RT}{z_i F} \ln \frac{a_i^o}{a_i^w} = \Delta_o^w \varphi_i^o + \frac{RT}{z_i F} \ln \frac{c_i^o}{c_i^w}$$

where $\Delta_o^w \varphi$ is the potential difference between the organic and the aqueous phase, c_i^o and c_i^w are the concentrations in the organic and water phases and $\Delta_o^w \varphi_i^o$ is the formal ion transfer potential, which can be determined experimentally [6].

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Table 1
Parameters for uninhibited and inhibited ion transfer.

	Uninhibited ion transfer	Inhibited ion transfer
Shift of E_p^{fwd} at increasing v	No	Yes
$E_p^{fwd} - E_p^{bwd} \approx \frac{59}{z_i} mV$ at 25 °C	Yes	No, higher with increasing v
$\frac{I_p}{\sqrt{v}} = \text{const.}$	Yes	Yes
$\frac{I_p^{bwd}}{I_p^{fwd}} = 1$	Yes	Yes

The different formal transfer potentials $\Delta_o^w \varphi_i'$ can be determined by measuring the half-wave potentials for the ion transfer reactions with cyclic voltammetry (CV) [7]:

$$\Delta_o^w \varphi_i^{1/2} - \Delta_o^w \varphi_i' = \Delta_o^w \varphi_{Me_4N^+}^{1/2} - \Delta_o^w \varphi_{Me_4N^+}'$$

where $\Delta_o^w \varphi_i^{1/2}$ and $\Delta_o^w \varphi_{Me_4N^+}^{1/2}$ are the measured half-wave potentials of the ion i and Me_4N^+ , respectively. The half-wave potentials can be determined by

$$\Delta_o^w \varphi_i^{1/2} = \frac{E_p^{fwd} + E_p^{bwd}}{2}$$

The standard transfer potential is dependent on the relative hydrophilicity/hydrophobicity and is related to the standard Gibbs energy of transfer $\Delta G_i^{w \rightarrow o}$ as follows [7]

$$\Delta G_i^{w \rightarrow o} = z_i F \Delta_o^w \varphi_i'$$

Likewise by analogy, the formal Gibbs energy of transfer can be defined by

$$\Delta G_i'^{w \rightarrow o} = z_i F \Delta_o^w \varphi_i'$$

The standard Gibbs energy of transfer refers to the transfer from pure water to pure organic solvent. Here, the transfer from water saturated with organic solvent to organic solvent saturated with water is reflected by the Gibbs energy of partition. However, in the case of low miscibility of water and DCE, the standard Gibbs energy of transfer is equal to the Gibbs energy of partition.

Lipophilicity expresses the relative affinity of solutes for an aqueous phase and an organic phase and is measured by the distribution behavior of solutes in a biphasic system. This can be described by the partition coefficient P_i , which is given with the organic phase as numerator, so that a positive value for $\log P_i$ reflects a preference for the organic phase.

$$\log P_i = -\frac{\Delta G_i^{w \rightarrow o}}{2.303 RT}$$

The correlation between peak current and scan rate is given by the Randles-Sevcik-equation

$$I_p^{fwd} = 0.4463 z_i F A c_i \left(\frac{z_i F}{RT}\right)^{\frac{1}{2}} D_i^{\frac{1}{2}} v^{\frac{1}{2}}$$

where A is the area of the interface (4.5 cm²) and D_i the diffusion coefficient. By varying the scan rate and plotting the peak current versus the square root of the scan rate the slope of the resulting line is proportional to the diffusion coefficient in a reversible system. Here, the transfer and the resulting current are realized across the water/dichloroethane interface, thus, obtaining transfer coefficients across the interface from the linear regression.

CV at large ITIES was used to study the transfer of selected highly diluted ILs across the water/DCE interface to evaluate their

electrochemical and their solvation properties. The structures of the selected ILs are shown in Fig. 1.

The focus is directed to the cations, so that an evaluation of their lipophilicity is given. Thus, ITIES will offer a novel tool to characterize the solubility of ILs in different solvents.

2. Experimental

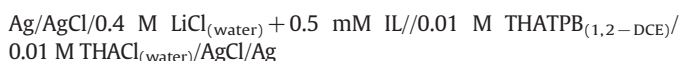
2.1. Chemicals

Lithium chloride (LiCl), tetramethylammonium chloride (TMACl), 1,2-dichloroethane (DCE) and tetraheptylammonium-tetraphenylborate (THATPB) were obtained from Sigma Aldrich (Munich, Germany). 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl) and 1-ethyl-3-methylimidazolium bromide ([EMIM]Br) were purchased from Solvent Innovation, now part of Merck (Darmstadt, Germany). 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄) and 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) were received from io-li-tec (Heilbronn, Germany). 1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM]OTf) was purchased from Merck (Darmstadt, Germany). Ultrapure water was used in all experiments. All chemicals were obtained in the highest available purity and were used as received.

2.2. Measurements

CV measurements were carried out by a PARSTAT 4000 from Princeton Applied Research, Ametek (Meerbusch, Germany) with VersaStudio 2.43.3 software and using Origin 8.1 for peak integration. A four-electrode system, consisting of two platinum wires as working electrodes and two Ag/AgCl (saturated KCl) electrodes as reference ones, were used. The cell was constructed in-house and is shown in Fig. 2. The area of the interface is 4.5 cm².

All measurements were performed at room temperature (about 23–25 °C), with both phases unstirred. CVs were recorded at scan rates of 4, 6, 8, 10, 12, 15 and 20 mV/s. The electrochemical cell can be written as follows:



where THATPB refers to the hydrophobic organic base electrolyte and LiCl to the aqueous phase. The cell potential scale was referenced to the absolute scale using the transfer of the tetramethylammonium cation (Me_4N^+) as an internal reference and correlating its transfer

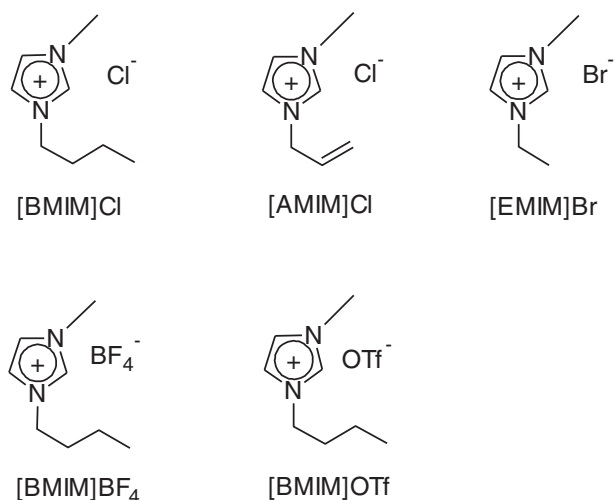


Fig. 1. Chemical structures of selected ionic liquids in this study.

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