

# Transfer of Ionic Liquids across the Interface between Two Immiscible Electrolyte Solutions

Sina Kummer, Wolfgang Ruth and Udo Kragl

Institute of Chemistry | University of Rostock, Albert-Einstein-Str. 3a | 18059 Rostock, Germany

## Introduction

Only a few fundamental electrochemical studies of ionic liquids at the interface between two immiscible electrolyte solutions (ITIES) have been reported to evaluate the electrochemical and solvation properties of typical ionic liquids [1]. The interface is formed between a hydrophilic electrolyte dissolved in water and a hydrophobic electrolyte dissolved in an organic solvent, for example 1,2-dichloroethane. The transfer of the 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 diffusion coefficients of ILs can be determined by cyclic voltammetry at large ITIES.

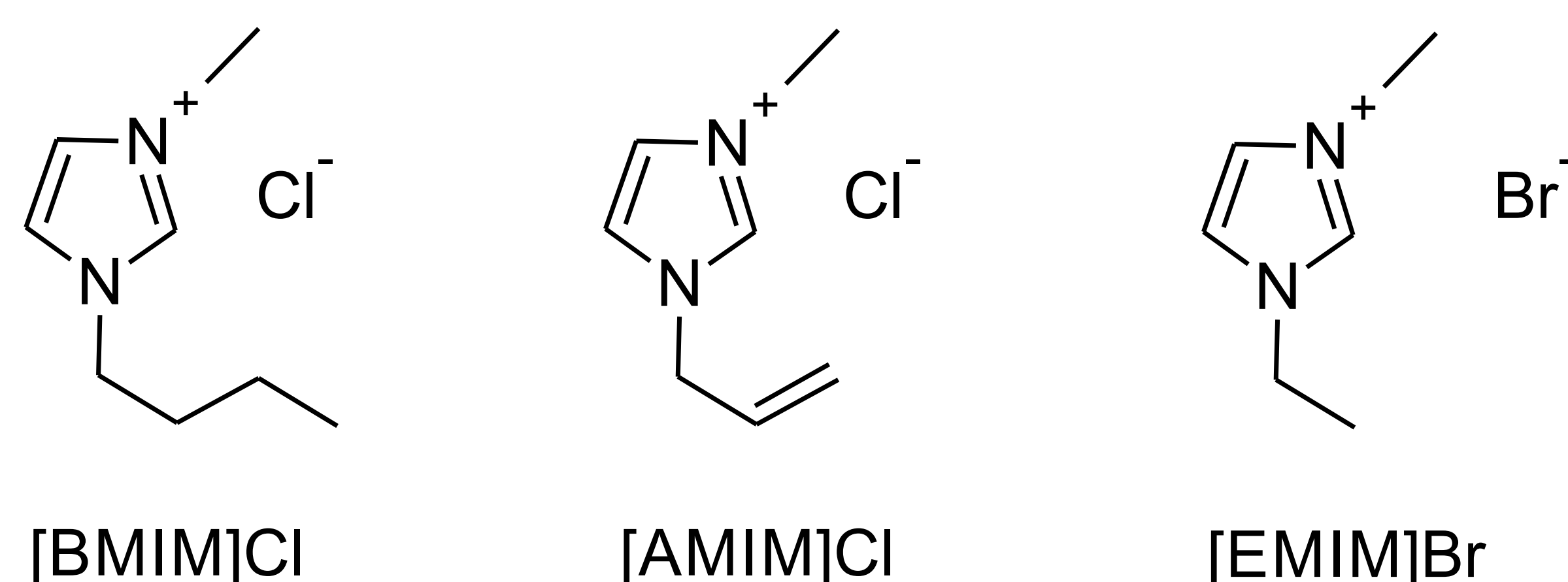


Fig. 1: Structure of tested ILs.

## Results

### Experimental Setup

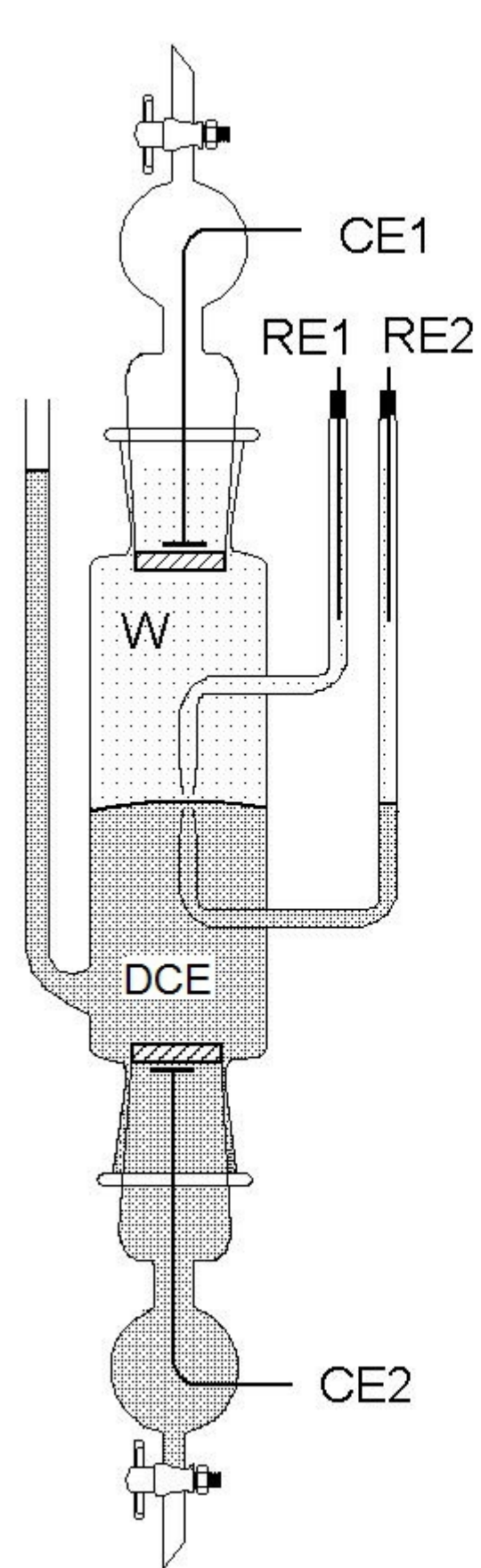


Fig. 2: Four-electrode cell.

The supporting electrolytes were solutions consisting of 0.4 M lithium chloride in water and 0.01 M tetraheptylammonium-tetraphenylborate (THATPB) in 1,2-dichloroethane (1,2-DCE). Ionic liquids (0.5 mM) were dissolved in the water phase. A four-electrode system with two platinum wires as working electrodes and two Ag/AgCl (saturated KCl) electrodes as reference ones were used. The electrochemical cell can be written as follows:

$\text{Ag/AgCl/LiCl}_{(\text{water})} + \text{IL} // \text{THATPB}_{(1,2\text{-DCE})} / \text{THACl/AgCl/Ag}$   
All measurements were performed at room temperature (about 24 °C), with both phases unstirred. Cyclic voltammograms were recorded at scan rates of 4-100 mV/s. The cell potential scale was referenced to the absolute scale of the transfer of the tetramethylammonium cation ( $\Delta_o^w \varphi_{\text{Me}_4\text{N}^+}^{\circ} = 0.16 \text{ V}$ ) as an internal reference by adding  $\text{Me}_4\text{N}^+$  to the aqueous phase after each measurement [1, 2].

### Cyclic voltammograms of IL transfer

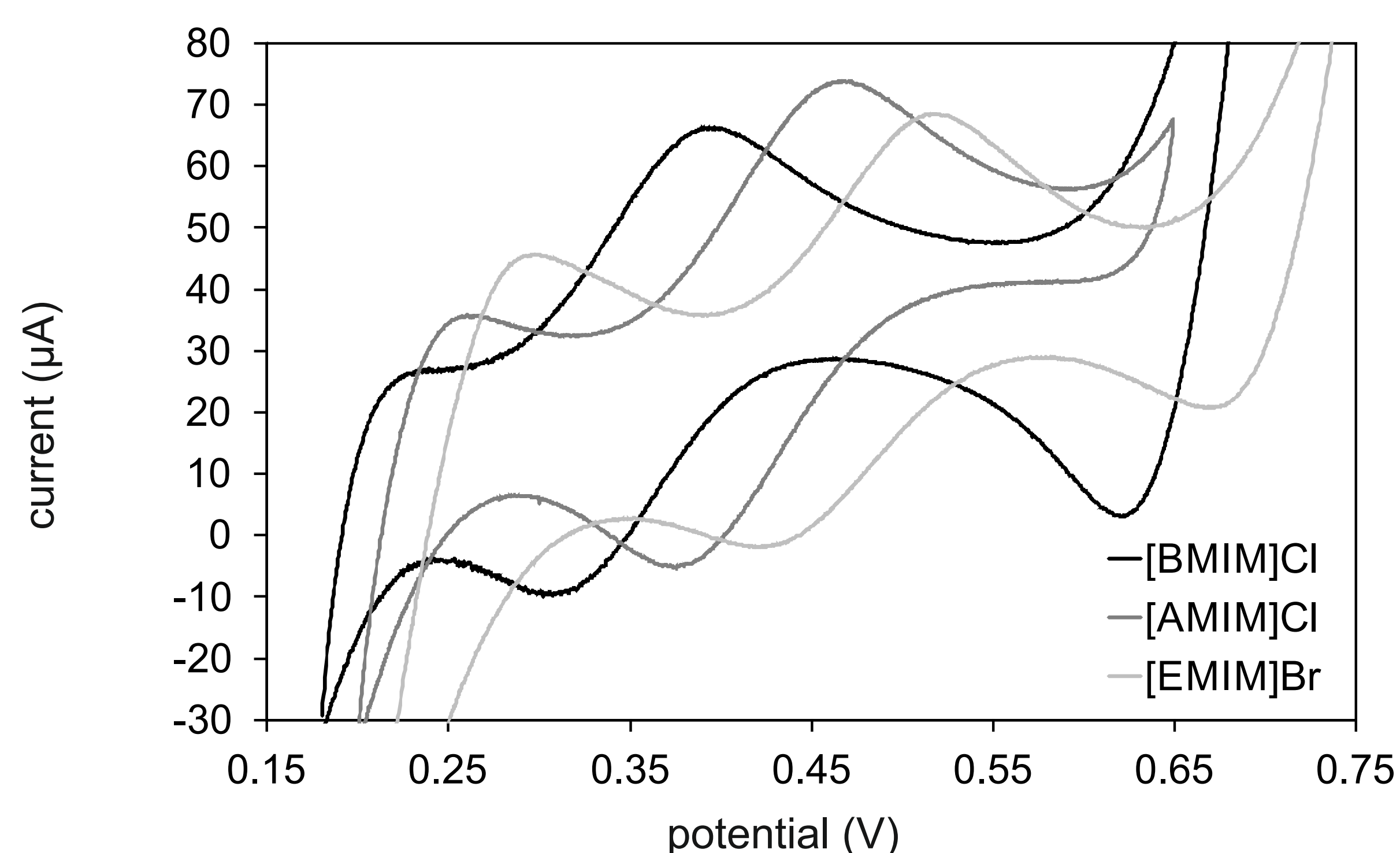


Fig. 3: Reversible transfer of ILs across ITIES at 4 mV/s scan rate. The current flow represents the transfer of the cation through the interface, mediated by a potential-driven process.

### Determination of relative lipophilicity

Standard transfer potentials of ILs at a polarized liquid-liquid interface give an indication of the relative lipophilicity due to a measure of the relative solvation properties of the transferring ionic species in each phase. As the applied potential is made more positive  $\varphi^w > \varphi^o$ , a cation may transfer from the aqueous phase to the organic phase or an anion may transfer in the opposite direction. The different formal potentials  $\Delta_o^w \varphi_i^{\circ}$  can be determined by measuring the half-wave potentials:

$$\Delta_o^w \varphi_i^{1/2} = E_p^{\text{fwd}} - ((E_p^{\text{fwd}} - E_p^{\text{bwd}})/2)$$

for the ion-transfer reactions with cyclic voltammetry [3]:

$$\Delta_o^w \varphi_i^{1/2} - \Delta_o^w \varphi_i^{\circ} = \Delta_o^w \varphi_{\text{Me}_4\text{N}^+}^{1/2} - \Delta_o^w \varphi_{\text{Me}_4\text{N}^+}^{\circ}$$

with  $\text{Me}_4\text{N}^+$  as internal reference ion. The standard transfer potentials are dependent on the relative lipophilicity

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

and are related to the standard Gibbs energy of transfer [4]:

$$\Delta G_i^{\circ, w \rightarrow o} = z \cdot F \cdot \Delta_o^w \varphi_i^{\circ}$$

### Determination of diffusion coefficients

The diffusion coefficient of a transferring species  $i$  at the ITIES is related to the recorded peak current by the Randles-Sevcik equation:

$$I_p = 0.4463 \cdot z \cdot F \cdot A \cdot c_i \cdot (z_i F / RT)^{1/2} D_i^{1/2} \cdot v^{1/2}$$

where  $I_p$  is the peak current,  $A$  the interfacial area (in this case  $A = 4.5 \text{ cm}^2$ ),  $c_i$  the bulk concentration,  $D_i$  the diffusion coefficient and  $v$  the potential scan rate.

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.

Table 1: Transfer potentials of ILs across ITIES with calculated lipophilicity and diffusion coefficients.

IL	$E_p^{\text{fwd}}$ [V]	$E_p^{\text{bwd}}$ [V]	T [K]	$\Delta G_i^{\circ, \alpha \rightarrow \beta}$ [kJ/mol]	$\log P_{\text{DCE}}^{\circ, i}$	$D_i$ [10 <sup>-9</sup> m <sup>2</sup> /s]
[BMIM]Cl	0.390	0.321	296.75	-2.12	0.37	2.58
[AMIM]Cl	0.459	0.384	297.25	4.54	-0.79	2.32
[EMIM]Br	0.513	0.437	297.75	8.20	-1.44	0.49

## Summary and Outlook

The reversible transfer of three ILs between water and 1,2-dichloroethane are shown. The partitioning of the ionic species between these two phases are calculated. An order can be given: [BMIM]<sup>+</sup> possesses the highest lipophilicity to go from water into the organic phase. [AMIM]<sup>+</sup> and especially [EMIM]<sup>+</sup> are hydrophilic. This fact is corroborated by the diffusion coefficients: [EMIM]<sup>+</sup> has the lowest value to go from water phase into 1,2-dichloroethane phase. On the one hand further steric cations could be tested, and on the other hand steric anions with simple cations could be proved. Therefore, adequate supporting electrolytes with resulting applicable potential window have to be probed.

- References: [1] Quinn, B.M., Ding, Z., Moulton, R., Bard, A.J., *Langmuir*, 2002, 18, 1734-1742.  
[2] Wandlowski, T., Marecek, V., Samec, Z., *Electrochimica Acta*, 1990, 35, 1173-1175.  
[3] Reymond, F., Steyaert, G., Carrupt, P.-A., Testa, B., Girault, H.H., *Helvetica Chimica Acta*, 1996, 79, 101-117.  
[4] Girault, H.H. In *Modern Aspects of Electrochemistry*; edited by Bockris, J.O'M et al. Plenum Press: NY, 1993; Vol. 25, p 1.

Scan this for pdf

