Electrochemistry Communications 48 (2014) 173–177

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

An unusual non-Tafel dependence for electron transfer reactions in ionic liquids at large electrode polarisations: Fiction or reality?

Alexei A. Kornyshev *, Lu-Peng Yang

Department of Chemistry, Imperial College London, SW7 2AZ London, United Kingdom

ARTICLE INFO

Article history:
Received 30 July 2014
Received in revised form 4 September 2014
Accepted 5 September 2014
Available online 16 September 2014

Keywords:
Ionic liquids
Electrochemical kinetics
Lattice saturation
Crowding
Current–voltage dependence

ABSTRACT

We speculate about the existence of a “square-root Tafel dependence” for simple one stage anodic/cathodic electron transfer reactions in ionic liquids. In this dependence, the logarithm of the current depends linearly on the *square-root* of electrode potential. The modified law is a consequence of ion crowding in the electrical double layer at high charges of the electrode. It may be expected that this effect may be observed for slow reactions at large electrode polarisations, yet not triggering electrochemical decomposition of ionic liquids, and only if diffusion limitations on the transport of reactants are absent.

1. Introduction

In electrochemistry the applied voltage is used as a driving force of reaction, by making the reaction free energy more negative [1]. For this to operate, the difference of electrostatic potential between the electrode and the position where the reactant is located must be substantial. To ensure this, concentrated buffer electrolytes are used to localize the voltage drop close to the electrode. Finer effects are known to take place, when it is not possible to localise the potential drop of the double layer solely between the electrode and reaction plane. This leads to the well known ψ '-effect, or Frumkin correction to current voltage characteristics [2–4].

Over the last decade electrochemists have taken great interest in the kinetics of electrochemical reactions in room temperature ionic liquids (RTILs) [5,6]. The motivation for replacing the electrolytic solution with solvent-free electrolyte is as follows: (i) RTILs can sustain higher voltages before their ions undergo electrochemical transformations than aqueous electrolytes, and the polarisation to drive the reaction of dissolved species can be made higher, speeding up the reaction kinetics (although they may not always beat organic solvents in this respect); (ii) RTILs are not volatile; (iii) due to strong Coulomb correlations in RTILs — ‘dense room-temperature ionic plasmas’, the phenomenon of overscreening can make the potential difference between the electrode and reaction plane *larger* than the potential drop across the whole double layer. This is expected to occur at low or moderate deviation from the potential of zero charge (pzc), but at least there the reaction rate will be amplified. These expectations are discussed in a recent review article [7].

Here, we will, however, focus on the limit of *large* deviations from the pzc, promoting higher reaction rates. At large electrode potentials the structure of the electrical double layer in RTILs is affected by the so-called crowding effect, because there is a limit on the maximum concentrations of ions, $c_{\max}$, which the counterions populating the double layer cannot exceed. Hence, counterions start to line up layer-by-layer, and unlike in the Gouy–Chapman theory, the characteristic thickness of the double layer starts to grow. In the context of RTILs this effect was put forward in Ref. [8], and analysed in detail in a series of reports [9–11]; experimental verification and approval by atomistic as well as coarse-grained molecular dynamic simulations have been reported in Refs. [12–17]; for a review see also the detailed discussion in Ref.[7]. Schematic drawing of double layer structures in overscreening and crowding modes is shown in Fig. 1.

When the rate-determining stage is the electron-transfer process across the interface, the cathodic or anodic currents of elementary redox-reactions in ordinary electrolytes at high large overvoltage are governed by the asymptotic Tafel law, in which the logarithm of the current depends linearly to the potential drop across the double layer, even if it is not at all confined between the electrode and reactant plane. We will show, however, that under the same conditions, in RTILs the logarithm of the current may instead assume a linear dependence on the square-root of the electrode potential. We denote this correlation “square-root Tafel law”. Note that, strictly speaking, we will deal here not with the dependence on the over potential, but on the electrode potential far from pzc and equilibrium.

---

* Corresponding author.
E-mail address: a.kornyshev@imperial.ac.uk (A.A. Kornyshev).

http://dx.doi.org/10.1016/j.elecom.2014.09.005

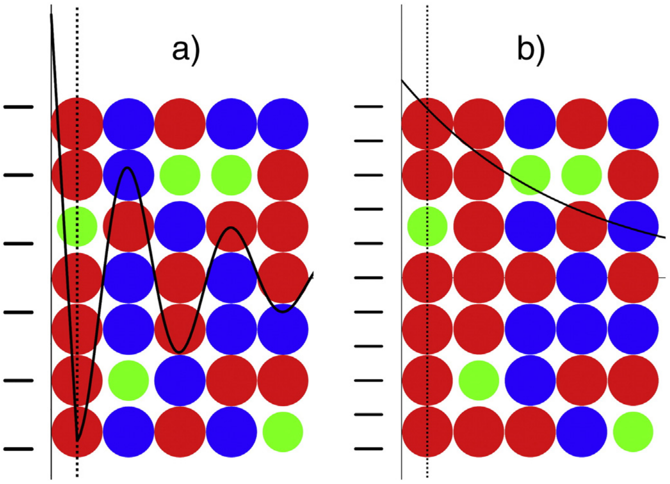

Fig. 1. A sketch of the double layer structure in ionic liquids near a negatively charged electrode under (a) overscreening and (b) crowding polarisation regimes. Red, blue and green spheres represent cations, anions and reacting species, respectively. Dotted line indicates the Helmholtz plane. Solid lines mimic the corresponding potential profiles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

This law will not be seen, if screened by the diffusion limiting current. Since the diffusion of ions in RTILs may be two orders of magnitude slower than in “ordinary” (aqueous) electrolytes, removal of diffusion limitations may be difficult. The use of rotating disc microelectrodes or other means to undermine diffusion limitations will be needed for experimental verifications of this manifestation of the peculiar structure of the electrical double layer in RTILs. This law could possibly be observed also at elevated temperatures, since electrochemical measurements with high precision in ionic liquids at over 200 °C have already been conducted[18].

2. Derivation of the “square-root Tafel dependence”

Consider for definiteness an anodic process, where anions are discharged at positively charged electrodes. For large voltages, the electric current density can be approximated by [19], $j = A \cdot (1 - j/j_d)c_r \cdot \exp\{\beta e[U - \Psi(U)]/k_BT\}$. Here, e is the elementary charge, U is the potential drop across the double layer, Ψ is the electrostatic potential on the reactant plane which itself is a function of U, c_r is the maximum possible concentration of reactants at the reaction plane, and j_d is the diffusion limiting current. The factor $(1 - j/j_d)$ which takes into account possible exhaustion of the reactants if they cannot rapidly replace those that have been converted into products, $0 < \beta < 1$ is the transfer coefficient for the anodic current, and the pre-factor A accommodates all the pre-exponential factors that are independent of electrode potential (say, electronic density and electronic tunnelling factor), as well as the factor $\exp\{-\beta e[U_0 - \Psi_0]/k_BT\}$ where U_0 and Ψ_0 are the values of U and Ψ at equilibrium.

Note that we assume that c_r is independent of the electrode potential. The potential dependence of c_r depends on the competition between the short range and electrostatic interactions of the reactants with the ions of the RTIL; such dependence, if present will therefore be ionic liquid specific [20].

Solving the above equation for j and using hereafter, for compactness of notation, dimensionless potentials (measured in units of thermal voltage k_BT/e which at room temperature is close to 26 mV), $u = eU/k_BT$, $\psi = e\Psi/k_BT$, we obtain,

$$j = \frac{A \cdot c_r \cdot e^{\beta[u-\psi(u)]}}{1 + \frac{1}{i_d} A \cdot c_r \cdot e^{\beta[u-\psi(u)]}}. \tag{1}$$

If the second term in the denominator is small, i.e. for very slow reactions (small values of A and large i_d), the reaction rate is determined by the electron transfer stage, and

$$j \approx A \cdot c_r \cdot e^{\beta[u-\psi(u)]}. \tag{2}$$

Note that these equations do not take into account migration limitations, which are expected to be unimportant in highly concentrated electrolytes such as RTILs. Furthermore these equations are based on a simplistic slow discharge theory. Corrections coming from the modern quantum electrochemistry will be considered in the Discussion.

So far there was nothing new in these expressions, and they apply to both ordinary aqueous buffer electrolytes and RTILs. Once we consider the asymptotic form of $\psi(u)$ at large electrode potentials valid for RTILs we will, however, get a new current–voltage law.

In order to evaluate $\psi(u)$ we need several assumptions. The first one utilizes the fact that in order to take part in the reaction the reactant ions must come very close to the electrode, so that the resulting electric field is constant in the gap between the electrode surface and the ‘reaction plane’. It is essentially the same as to assume the reactants sitting on the ‘Helmholtz plane’. Hence, due to the Gauss theorem [21],

$$\varepsilon_H \frac{\frac{k_BT}{e}[u - \psi(u)]}{d} = 4\pi\sigma \tag{3}$$

where ε_H is the effective dielectric constant in the compact layer (for RTIL expected to be on the order of 2), d is its thickness, and σ is the surface charge density on the electrode (hereafter we use Gaussian units). To complete the task of evaluating $\psi(u)$ we need to find the $\sigma(u)$-dependence.

Reference [8] has presented a mean field theory description that resulted in an analytical formula for $\sigma(u)$ for all electrode potentials, as well as a simple expression for it in the large-voltage limit. However, it was shown in the same report that based on the charge conservation law, the limiting behaviour of $\sigma(u)$ can be obtained without a model, using the scaling-type analysis, which we reproduce below.

In the crowding regime,

$$\sigma = -ec_{\max} l_c \tag{4}$$

where l_c is the effective thickness of the crowded region. Going for a moment back to dimensional potential and electric field, we may estimate the electric field at the Helmholtz plane, E, as $E \approx -\Psi/l_c$. On the other hand, $E = 4\pi\sigma/\varepsilon$, where ε is the effective dielectric constant of the liquid (for RTILs ~10) [22,23]. Hence,

$$l_c \approx -\varepsilon\Psi/4\pi\sigma. \tag{5}$$

Inserting this expression for l_c into Eq. (4), we get $\sigma = ec_{\max}\varepsilon\Psi/4\pi\sigma$, and thus

$$\sigma = \sqrt{ec_{\max}\varepsilon\Psi/4\pi}. \tag{6}$$

To the accuracy of the factor of $\sqrt{2}$, the r.h.s. of Eq. (6) coincides with the expression given by the mean-field theory. Returning to dimensionless potentials, and combining Eqs. (6) and (3) we obtain $\varepsilon_H(u - \psi(u))/d = \sqrt{(4\pi e^2 c_{\max}/k_BT)\varepsilon\psi}$.

It will be convenient to rearrange this last equality, using two parameters: the quantity equivalent to the inverse Debye length,

$$\kappa \equiv \frac{1}{L_D} = \sqrt{\frac{4\pi e^2 c_0}{\varepsilon k_BT}}, \tag{7}$$