



Simultaneous characterisation of electrode kinetics and electrolyte properties in ionic liquids using a rotating disc electrode

David Lloyd, Tuomas Vainikka, Sönke Schmachtel, Lasse Murtomäki*, Kyösti Kontturi

Aalto University, Department of Chemistry, PO Box 16100, 00076 Aalto, Finland

ARTICLE INFO

Article history:

Received 10 October 2011

Received in revised form 21 February 2012

Accepted 24 February 2012

Available online 11 March 2012

Keywords:

Deep eutectic solvents

Ionic liquids

Impedance spectroscopy

Rotating disc electrode

ABSTRACT

In this work, simultaneous characterisation of conductivity, viscosity and heterogeneous kinetics is demonstrated in a deep eutectic solvent based on choline chloride and ethylene glycol, using concurrent steady state voltammetric and impedance measurements at a rotating disc electrode. A theoretical treatment based on post-experimental correction of ohmic losses is shown to be reliable. The parameters determined at 25 °C are: standard rate constant of electron transfer $k^0 = 10 \pm 1 \times 10^{-4} \text{ cm s}^{-1}$, charge transfer coefficient $\alpha = 0.39 \pm 0.03$, formal potential $E^{0'} = 0.430 \pm 0.005 \text{ V}$ vs. Ag/AgCl, conductivity $\kappa = 10.1 \pm 0.3 \text{ mS cm}^{-1}$, dynamic viscosity $\eta = 37 \pm 3 \text{ mPa s}$, diffusion coefficient of Cu^{2+} $D_0 = 1.32 \pm 0.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and Stokes radius of the Cu^{2+} complex $R_H = 0.33 \text{ nm}$.

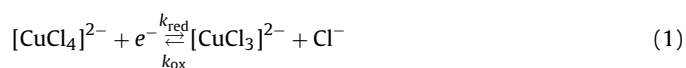
Conventional conductivity and rheometric measurements were also performed. The electrolyte conductivity and dynamic viscosity were $8.0 \pm 0.3 \text{ mS cm}^{-1}$ and $41 \pm 3 \text{ mPa s}$ respectively at 25 °C. These values compare well with the values determined using electrochemical methods. The deep eutectic solvent used has been shown to exhibit conductivity and viscosity comparable to modern ionic liquids based on discrete anions. The Stokes radius of the $[\text{CuCl}_4]^{2-}$ complex formed confirms the similarity of these deep eutectic solvents to basic chloroaluminate ionic liquids.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Deep eutectic solvents (DES) are a class of materials, similar to chloroaluminate ionic liquids that are formed by complexation of the anion in a halide salt by means of hydrogen bonding. The prototypical salt is choline chloride (ChCl or (2-hydroxyethyl)trimethylammonium chloride) and typical hydrogen bond donors are either amines [1], diols [2] or carboxylic acids [3]. DES based on these combinations show a significant capacity to dissolve metal chlorides, making them simple to use for studies of metal chloro complex electrochemistry and electrodeposition in particular [4]. The primary advantages of DES, compared to regular ionic liquids, are the extremely low cost of the precursors and their general biodegradability.

In a previous paper we presented kinetic parameters describing the $\text{Cu}^{2+}/\text{Cu}^+$ redox reaction shown in Eq. (1) in a DES consisting of ethylene glycol and choline chloride [5], which is commonly referred to as ethaline.



That work was based on stationary electrode techniques and showed that electron transfer was rate determining, i.e., that the homogeneous reactions relating to the loss or acquisition of a chloride ligand were not apparent. In this paper the benefits gained from using hydrodynamic techniques in the study of electrochemical behaviour in ionic liquids are illustrated, specifically when using a rotating disc electrode (RDE). The RDE is a well-established experimental technique with a long history in the study of electrochemical systems [6]. The main mode of operation is to determine current as a function of potential under steady-state mass transfer, since such a system is relatively trivial to describe mathematically and to acquire experimentally. A wide range of complicated reaction mechanisms can be readily characterised using this technique, for instance coupled heterogeneous and homogeneous reactions [7]. In many of these cases analytical expressions describing the I - E relationship exist or can be readily derived. This greatly simplifies the process of identifying and characterising a mechanism that describes the observed behaviour.

An additional benefit when using a RDE is that the hydrodynamic characteristics of the electrolyte, i.e., the kinematic viscosity, manifest themselves in the experimental data. This can be used to determine the Stokes' radii of the diffusing species with high precision, since the necessary measurements can be performed concurrently under identical conditions. In combination with other

* Corresponding author. Tel.: +358 9 470 22575; fax: +358 9 470 22580.
E-mail address: lasse.murtomaki@aalto.fi (L. Murtomäki).

techniques, such as UV–vis, this allows a more reliable comparison of electrolyte systems, since there is less ambiguity regarding speciation.

The use of RDE techniques in the study of ionic liquids is potentially hindered by their viscous nature and poor conductivity [8]. This work illustrates that these limitations in no way prevent the accurate characterisation of a fast heterogeneous reaction. Since the technique is based on steady state behaviour there are two strategies available to deal with solution resistance. The first is to perform compensation in real time using analogue feedback circuitry. In this case the slow measuring speeds used during RDE measurements place minimal demands upon the dynamic performance of the potentiostat and reference electrode. It is then possible to purposefully restrict the bandwidth of the potentiostat and thereby reduce noise and the risk of instability from feedback circuitry. Alternatively, it is possible to perform complete compensation of solution resistance after the experiment has been carried out by simply subtracting the product of the measured current and the solution resistance from the applied potential; this is not possible for transient techniques such as cyclic voltammetry.

2. Theory

The conventional method of interpreting data measured at an RDE is to develop a Koutecký–Levich plot, viz I^{-1} vs. $\omega^{-1/2}$, where I is the current and ω is the angular frequency of rotation. For a quasi-reversible reaction the plot should be linear and the intercept at the ordinate axis gives the kinetic current, I_k . Thereafter a plot of $\ln(I_k)$ vs. potential can be used to determine the equilibrium potential E_{eq} , the standard rate constant k^0 and the charge transfer coefficient α .

An alternative approach, made possible by the digital era, is to perform a direct fit of the I – E relation measured during a single voltammogram. At the steady-state, the surface concentrations of the reacting species are [9]:

$$C_O^s = C_O^* + \frac{I}{nFAD_O/\delta_O}; \quad C_R^s = C_R^* - \frac{I}{nFAD_R/\delta_R} \quad (2)$$

where C^s and C^* are the surface and bulk concentrations of O, the oxidised species or R, the reduced species, D is the diffusion coefficient of O or R, δ is the diffusion layer thicknesses and all other symbols have their usual meaning. These can be substituted into a kinetic model of choice, such as the Butler–Volmer equation, and Eq. (3) results [10]; k_{red} and k_{ox} refer to the potential rate constants of reduction and oxidation, respectively:

$$I = \frac{nFA(k_{ox}C_R^* - k_{red}C_O^*)}{1 + k_{red}\delta_O/D_O + k_{ox}\delta_R/D_R} = \frac{I_k}{1 + k_{red}\delta_O/D_O + k_{ox}\delta_R/D_R} \quad (3)$$

$$k_{ox} = k^0 e^{(1-\alpha)f(E_{eff}-E^0)}; \quad k_{red} = k^0 e^{-\alpha f(E_{eff}-E^0)}$$

where $f = zF/(RT)$ and $E_{eff} = E - R_s I$. Accurate determination of I_k using the Koutecký–Levich plot requires real time compensation of the ohmic loss, which will scale with current and hence the rotation speed. If the value of the solution resistance R_s is known from, say, impedance measurements, the effective potential, in k_{red} and k_{ox} can be calculated when Eq. (3) is fitted to experimental data. Although a fit requires prior determination of the diffusion coefficients, it is not a problem since they can easily be measured with transient techniques [5]. A fit then returns the value of E^0 , k^0 , α and the bulk concentrations.

Alternatively, the formulation utilising limiting currents provides a more robust estimate of the kinetic parameters by eliminating any error in the values of the diffusion coefficients or kinematic viscosity. Because the limiting currents are [9]

$$I_{l,c} = \frac{-nFAD_O}{\delta_O C_O^*}; \quad I_{l,a} = \frac{nFAD_R}{\delta_R C_R^*} \quad (4)$$

Eq. (3) can be converted using Eq. (4) to

$$I = \frac{k_{ox}C_R^* - k_{red}C_O^*}{(nFA)^{-1} - k_{red}C_O^*/I_{l,c} + k_{ox}C_R^*/I_{l,a}} \quad (5)$$

Using either approach, the limiting case of infinite rotation speed is the kinetic current I_k shown in Eq. (3). This can, in principle, be fitted to kinetic currents, determined in the normal manner from the Koutecký–Levich equation.

From the hydrodynamic theory [11] the thickness of the diffusion boundary layer is defined as $\delta = 1.61D^{1/3}\omega^{-1/2}\nu^{-1/6}$, where ν is the kinematic viscosity. Combining this with Eq. (4) thus provides a means to estimate the dynamic viscosity η from the limiting current. Furthermore, the hydrodynamic radius r_H of the reacting species can be estimated using the Stokes–Einstein equation, $D = k_B T / (6\pi\eta r_H)$, where k_B is the Boltzmann constant and all other symbols have their usual meaning.

In addition to characterising the kinetics using the methods outlined above, it is also possible to perform Electrochemical Impedance Spectroscopy (EIS) measurements at the RDE. This has, for instance, been discussed by Boillot et al. [12] for an aqueous potassium ferri/ferrocyanide system. The observed behaviour is similar to that described by the Randles' equivalent circuit at a stationary electrode, with two important differences. Firstly, the surface concentrations during the entire EIS measurement are unambiguously defined at an RDE, as shown in Eq. (2). Secondly, at sufficiently low AC frequencies the impedance deviates from the behaviour of a stationary electrode, and replacement of the infinite length Warburg element with a finite-length Warburg element is required:

$$Z_{w,s} = \frac{R_{ct}}{\sqrt{j\omega_{EIS}}} \left(\frac{k_{red} \cdot \tanh(\delta_O \sqrt{j\omega_{EIS}/D_O})}{\sqrt{D_O}} + \frac{k_{ox} \cdot \tanh(\delta_R \sqrt{j\omega_{EIS}/D_R})}{\sqrt{D_R}} \right) \quad (6)$$

where ω_{EIS} corresponds to the angular frequency of the AC excitation and j is the imaginary unit ($j^2 = -1$). At sufficiently high AC frequencies the diffusion impedance is described by the Warburg impedance, i.e., when $\tanh(\delta \sqrt{j\omega_{EIS}/D}) \approx 1$.

The charge transfer resistance, R_{ct} , is given by Eq. (7) [10,13]:

$$R_{ct} = \frac{RT}{n^2 F^2 A} \cdot \frac{1}{(\alpha k_{red} C_O^s + (1-\alpha) k_{ox} C_R^s)} \quad (7)$$

In this work the double layer capacitance has been approximated by a constant phase element. The impedance of a constant phase element is given by Eq. (8).

$$Z_{CPE} = \frac{1}{(j\omega)^n Y_0} \quad (8)$$

where n is the frequency exponent and Y_0 the standard admittance. The total impedance response is determined by combining the elements described above as shown in Eq. (9)

$$Z = R_s + \left(\frac{1}{Z_{CPE}} + \frac{1}{R_{ct} + Z_{w,s}} \right)^{-1} \quad (9)$$

Newman [14] has derived the following simple relation between observed solution resistance, R_s , and conductivity, κ , for a disc electrode with the radius of a provided that the reference electrode is placed infinitely far from the disc surface.

$$R_s = (4\kappa a)^{-1} \quad (10)$$

Newman also illustrated that for finite electrode separation distances of even a few centimetres the deviation of the observed solution resistance from the limiting value is only around 5%. Hence

Download English Version:

<https://daneshyari.com/en/article/188737>

Download Persian Version:

<https://daneshyari.com/article/188737>

[Daneshyari.com](https://daneshyari.com)