

IONIC LIQUID-BASED, LIQUID-JUNCTION-FREE REFERENCE ELECTRODE

Dimitrije Cicmil¹, Salzitsa Anastasova¹, Andrew Kavanagh¹, Dermot Diamond^{1*}, Ulriika Mattinen², Johan Bobacka², Andrzej Lewenstam², Aleksandar Radu^{3*&}

¹CLARITY Centre for Sensor Web Technologies, National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland

²Åbo Akademi University, Process Chemistry Centre, Laboratory of Analytical Chemistry, and Centre for Process Analytical Chemistry and Sensor Technology ‘ProSens’, Biskopsgatan 8, FI-20500, Åbo/Turku, Finland

³School of Pharmacy and Biomedical Sciences, University of Portsmouth, Portsmouth, UK

[&]During the execution of this work, AR was a staff member of CLARITY Centre

*To whom the correspondence should be addressed:

dermot.diamond@dcu.ie, aleksandar.radu@port.ac.uk

Abstract

In this paper, we describe a new type of polymer membrane-based reference electrode (RE) based on ionic liquids (ILs), in both liquid-contact (LCRE) and solid-contact reference electrode (SCRE) forms. The ILs used were bis(trifluoromethane sulfonyl)amid with 1-alkyl-3-methylimidazolium as well as phosphonium and ammonium cations. In addition to their charge stabilisation role, it was found that the ILs also functioned as effective plasticizers in the PVC matrix.

The LCREs and SCREs were prepared using the same design as their corresponding indicator electrodes. LCREs were prepared by casting in glass rings while SCREs were prepared on platforms made using screen-printing technology, with poly(3-octylthiophene-2,5 diyl) (POT) as the intermediate polymer. After potentiometric characterization of the response mechanism, the practical performance of the REs was studied using potentiometric titrations (Pb^{2+} and pH), and characterised using cyclic voltammetry and impedance spectroscopy. All results were compared via parallel experiments in which the novel RE was substituted by a conventional double junction Ag/AgCl reference electrode.

The mechanism of response is most likely based on a limited degree of partitioning of IL ions into the sample thereby defining aquo-membrane interfacial potential. Despite their simple nature and construction, the REs showed excellent signal stability, and performed well in the analytical experiments. The identical mode of fabrication to that of the equivalent indicator (or Ion-Selective) electrode (ISE) will facilitate mass-production of both indicator *and* reference electrode using the same fabrication line, the only difference being the final capping membrane composition.

Keywords: reference electrode, polymer membrane, ion selective electrode, ionic liquid, electrochemical sensors, potentiometry, cyclic voltammetry, impedance spectroscopy

Introduction

In a recent *Analytical Chemistry* editorial, the development of low-cost, low power chemo/bio-sensing devices capable of monitoring our environment much more extensively and frequently than is now possible was highlighted as possibly the next grand challenge for analytical chemists [1]. Due to their relative simplicity, electrochemical sensors are promising candidates that could contribute significantly to progress in addressing this above challenge.

In particular, ion-selective electrodes now can routinely produce excellent detection limits in the ppb range, and this, coupled with their general robustness and virtually zero power demand, and compatibility with mass-production techniques, makes them interesting candidates for integration into wireless sensing networks [2]. This combination of qualities is essential for the practical realisation of widely-dispersed chemical sensor networks. However, while we have witnessed exciting breakthroughs in the performance of these sensors under controlled laboratory conditions, replicating this under real conditions has proven very difficult, and much of the work has been abandoned after publication in the scientific literature. One of the reasons for this lies in the fact that practical applications of devices requires a broader engagement and collaboration with the engineering community. For example, a collaborative effort between chemists, mechanical and electronic engineers has recently resulted in a miniaturised, autonomous wireless-sensor for environmental monitoring [2].

Another (often ignored) factor inhibiting progress is the unsatisfactory robustness of reference electrodes (REs). While there are many examples of designs and application of reference electrodes in sensing devices, they are often limited in terms of design and experimental protocol. Therefore research leading towards simpler, cheaper and more robust REs is critical if the progress is to happen.

A review by Bakker nicely outlined several concepts for making reference electrodes based on hydrophobic materials [3]. Some of the most promising are based on the response mechanism of ISEs, as defined by the phase boundary potential (E_{PB}) equation:

$$E_{PB} = \frac{RT}{z_1 F} \ln \frac{k_1 a_1}{\gamma_1 [I^{z_1}]} \quad (1)$$

where a_1 is the activity of an ion of charge z_1 in the sample phase boundary, γ_1 , and $[I^{z_1}]$ are the activity coefficient and the concentration of the free ion I^{z_1} in the organic membrane phase boundary, and R, T, and F are the gas constant, the absolute temperature, and the Faraday constant. The E_{PB} in this system is defined by a degree of partition of the lipophilic electrolyte from the membrane into the sample. This approach is well accepted by the sensor research community and various REs [4-7] and entire sensing systems for applications have been described [8]. For example, Horvai has suggested REs based on doping traditional plasticized PVC membranes with lipophilic electrolytes [9]. Another interesting approach is using a membrane responsive to a highly charged electrolyte and having some variable amount of this electrolyte in the sample [10]. Since the slope is inversely proportional to the electrolyte charge the E_{PB} is practically zero, and independent on the ion concentration. In other one, conduction polymers were doped by pH buffer ligands get to high pH buffer capacity of the CP films with this constant potential of the films in bathing solutions with lower pH buffer capacity [11]. It was shown that these films can be successfully used as solid-contact for ion-selective electrodes with plastic membranes.

Recently, ionic liquids (ILs) were suggested as very promising materials for the preparation of very simple ‘liquid-junction’-free REs [12]. They are utilized both as the solvent for AgCl, and as the salt bridge [13]. Because of their relative ease of preparation, and potential for tailoring properties, these materials present tremendous opportunity to design miniature and simple REs.

Another important challenge in designing REs is to ensure that their fabrication is compatible with mass-production techniques. To realise truly low-cost potentiometric sensors, the production of both the ISE *and* the RE must be simple and cost effective. Ideally, the fabrication of both ISEs and REs should be compatible with the same production line with minimal adjustments.

In this paper we describe an approach in development of REs that employs partially soluble ILs to define the E_{PB} at the PVC membrane – sample boundary. Partitioning of the IL ions creates conditions under which the membrane contains a relatively large concentration of ions that are also present in the aqueous phase. The potential of the membrane is therefore defined by Equation 1. As the membrane matrix is the only source of these ions, and they have limited aqueous solubility, the concentration ratio of ions in the sample and in the membrane should remain constant, and hence maintain a constant E_{PB} . Another promising feature of this RE concept is that the ISE and the RE can be fabricated using exactly the same technologies. Both electrodes are prepared on the same platform prepared using screen-printing technology and a conductive polymer as the ion-to-electron transducer. The only difference between the two electrodes is in the formulation of the capping membrane cocktail. The ISEs are prepared using traditional plasticized PVC membranes doped with an ionophore and ionic sites, while the REs are prepared using PVC plasticized with an IL. The latter therefore has a dual role – PVC plasticizer and lipophilic electrolyte that provides a stable E_{PB} .

Experimental

Materials and methods

Ionic liquids as shown in Table 1 were synthesized *in house*. They all contain bis(trifluoromethanesulfonyl) amide [NTf₂]⁻ anion. We also used a family of 1-Alkyl-3-methylimidazolium [C_rmim]⁺ cations, (wherein r represents various side chains as indicated in Table 1), as well as phosphonium ([P_{6,6,6,14}]⁺, [P_{4,4,4,14}]⁺) and ammonium [N_{1,8,8,8}]⁺ cations.

Table 1. Cations and anions used to prepare the ILs used in this work.

<i>IUPAC name</i>	<i>Short</i>	<i>Structural formula</i>
Bis(trifluoromethane sulfonyl)amide	[NTf ₂] ⁻	
1-ethyl-3-methylimidazolium	[C ₂ mim] ⁺	
1-butyl-3-methylimidazolium	[C ₄ mim] ⁺	
1-hexyl-3-methylimidazolium	[C ₆ mim] ⁺	
1-octyl-3-methylimidazolium	[C ₈ mim] ⁺	
1-dodecyl-3-methylimidazolium	[C ₁₂ mim] ⁺	
tributyl(tetradecyl)phosphonium	[P _{4 4 4 14}] ⁺	
triethyl(tetradecyl)phosphonium	[P _{6 6 6 14}] ⁺	
N-methyl-N,N-dioctyloctan-1-ammonium	[N _{1 8 8 8}] ⁺	

All other used chemicals were purchased from Methrom as Selectophore grade, and used as received. Reference electrode membranes were prepared by dissolving 160 mg of IL and 80 mg of polyvinyl chloride (PVC) in 3 mL of THF. The pH-selective electrode cocktail was prepared by dissolving 5 mmol/kg of sodium tetrakis-[3,5-bis(trifluoromethyl) phenyl] borate (NaTFPB), 15 mmol/kg of Hydrogen Ionophore II (H II), 33 wt% of poly(vinylchloride) (PVC) and 65 wt% of 2-nitrophenyl octyl ether (o-NPOE) in 3 ml of unhydrated tetrahydrofuran (THF). The cocktail for the Pb²⁺-selective membrane was prepared by dissolving 5 mmol/kg NaTFPB, 15 mmol/kg Pb ionophore IV, 32 wt% PVC, and 66 wt% of DOS in 3 mL THF. Two types of reference electrodes (REs) were prepared as follows.

Liquid-contact reference electrodes (LCREs) were made by casting the cocktails into a 22 mm i.d. glass ring fixed to a glass plate. After THF evaporation, an elastic membrane of ~200 μm thickness remains. Electrodes were fabricated by punching 6 mm diameter discs from the parent membrane and attaching them to the end of a 2 cm length of PVC tubing (3.2 mm i.d.) using PVC/THF adhesive. The PVC tubing was then attached to a 1 ml pipette tip and filled with the inner electrolyte solution. The inner reference electrode was a Ag/AgCl electrode immersed in 10⁻³M KCl inner filling solution.

Solid-contact reference electrodes (SCREs) were based on *in house* prepared platforms made using a DEK 248 screen printer. Ag-based ink was first used to print the contact track onto the polyethylene terephthalate (PET) base (thickness ca. 175 μm). The printed silver inks were cured in an oven at 120⁰C for 20 min. Carbon-based ink was then used to print the electrode sub-layer over one end of the silver track. The printed carbon inks were cured for 15 min at 150⁰C. An insulator (Electrodag 452 SS, an acrylate based UV cured photoresist) was then printed on top, covering everything but a small area of the electrode and the far end of the silver track.

All SC ISEs and SCREs were made using the following protocol. An intermediate polymer layer composed of poly(3-octylthiophene-2,5 diyl) (POT) was first deposited on all screen-printed electrodes by drop-casting using 2.5mM POT solution in chloroform. **Figure 1** shows the process of platform preparation (left), deposition of polymer membranes, and finished electrodes.

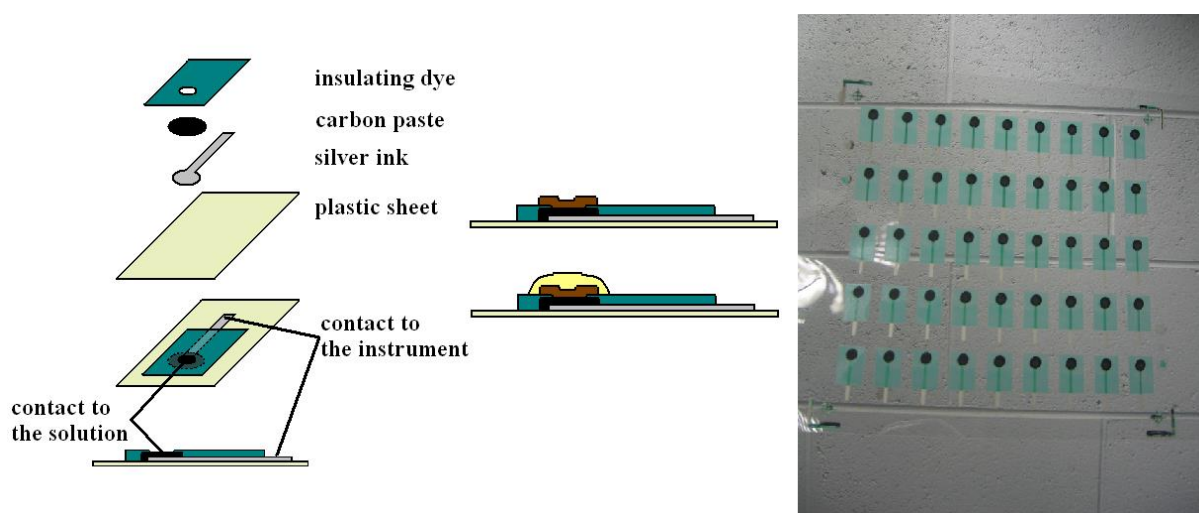


Figure 1. Preparation of platform by screen-printing (left) used to prepare indicator and reference electrode by drop casting (middle). A layer of POT (plum) is first cast on carbon electrode (black). PVC-based membrane (yellow) is then cast on top of POT layer. An array of prepared electrodes is presented on the right. Prior to use desired number of electrodes is cut and conditioned appropriately.

At this stage, sensors designated as REs had the RE PVC-cocktail drop-cast on top of the dried POT layer. Sensors were designated as pH- or Pb^{2+} -selective electrodes had the corresponding PVC cocktails drop-cast in a similar manner on the dry POT layer. Prior to use, the pH-selective electrodes were conditioned overnight in a universal buffer solution (10^{-3}M citric acid, boric acid and KH_2PO_4 ; pH=3.5) while the REs were conditioned for two hours in 10^{-3}M KCl. Pb^{2+} -selective electrodes were conditioned using a two-staged protocol. Electrodes were first conditioned overnight in 10^{-3}M PbNO_3 followed by conditioning for 24 hours in a solution of 10^{-9}M PbNO_3 at pH=4.

Potentiometric measurements were performed at room temperature (21°C) using a Lawson Labs Inc. EMF 16 electrode monitor (3217 Phoenixville Pike Malvern, PA 19355, USA). EMF measurements were conducted in stirred solutions using a magnetic stirring plate. For comparative measurements, conventional a Ag/AgCl reference electrode (Metrohm, 6.0729.100) with 1M LiOAc as bridge electrolyte was used in parallel experiments. All values were corrected for liquid-junction potentials using the Henderson formalism and ion activities were calculated according to the Debye-Hückel approximation.

Results and discussion

Characterization

The reference electrode studied in this work has a very simple two-component polymer capping membrane composed of PVC and IL.

Finding suitable candidates that can both plasticise the PVC polymer, and provide the critically important constant phase boundary potential is a significant challenge, since the IL has to be partially soluble in water as described earlier. ILs have previously been used to plasticize polymers in polymeric sensing devices [14-16]. Apart from few examples, mechanical properties of obtained membranes were in most cases satisfying, and functional membranes were prepared [17]. In this work, all IL-based membranes were prepared from only two components – PVC and IL in a traditional composition of 33% of PVC and 67% of plasticizer (IL). Cocktails were either cast in a glass ring (for LCREs) or drop-cast on the in-house fabricated platform (for SCREs). All membranes prepared using both approaches were found to have satisfactory mechanical properties.

Marciniak reported detailed study of IL solubility, and calculated Hildebrand's solubility parameters for 18 different ILs using inverse gas chromatography [18]. Relevant to this work

were his observations on the anion influence on the solubility parameter for ILs based on 1-alkyl-3-methyl-imidazolium cations [Rmim]⁺. He reported that the solubility decreases in the following order: [Cl]⁻ > [NTf2]⁻ > [CF₃SO₃]⁻ > [OcSO₄]⁻ > [PF₆]⁻ > [BF₄]⁻ > [TOS]⁻ > [SCN]⁻ > [MDEGSO₄]⁻ > [TFA]⁻. In other words the most soluble ILs were the ones based on [Cl]⁻, followed by [NTf2]⁻, whilst the most insoluble ones were based on [TFA]⁻. On the other hand, according to Kakiuchi, the solubility of imidazolium decreases with increasing the number of C atoms in position 1 [19]. This is expected due to the increase in lipophilicity of the sidechain in position 1 in 1-alkyl-3-methyl-imidazolium cations. Therefore ILs based on [Rmim]⁺ and [NTf2]⁻ are excellent candidates to form an IL whose ions are only partially soluble in water, and therefore should be good candidates for producing a stable membrane boundary potential [3, 9]. Partitioning of both ions is important in order to avoid ion exchange effects. If one ion from the IL exchanges with a sample ion of the same charge while the counterion does not, the membrane starts to exhibit ion-exchange properties, rendering the membrane responsive to that ion.

In our experiments, we used a series of imidazolium-based [NTf2]⁻ ILs, as well as [P₆₆₆₁₄][NTf2] and [N₁₈₈₈][NTf2] to prepare SCREs. We tested the stability of the resulting RE signal by immersing electrodes in 0.1 M KCl, 10⁻⁴ M KCl, 10⁻⁴ M NaCl, 0.1 M NaCl and 0.1 M KCl, which enabled the effects of large sample ion concentration differences, ionic strength effects and variable ion mobility to be investigated. The results are shown in Figure 2.

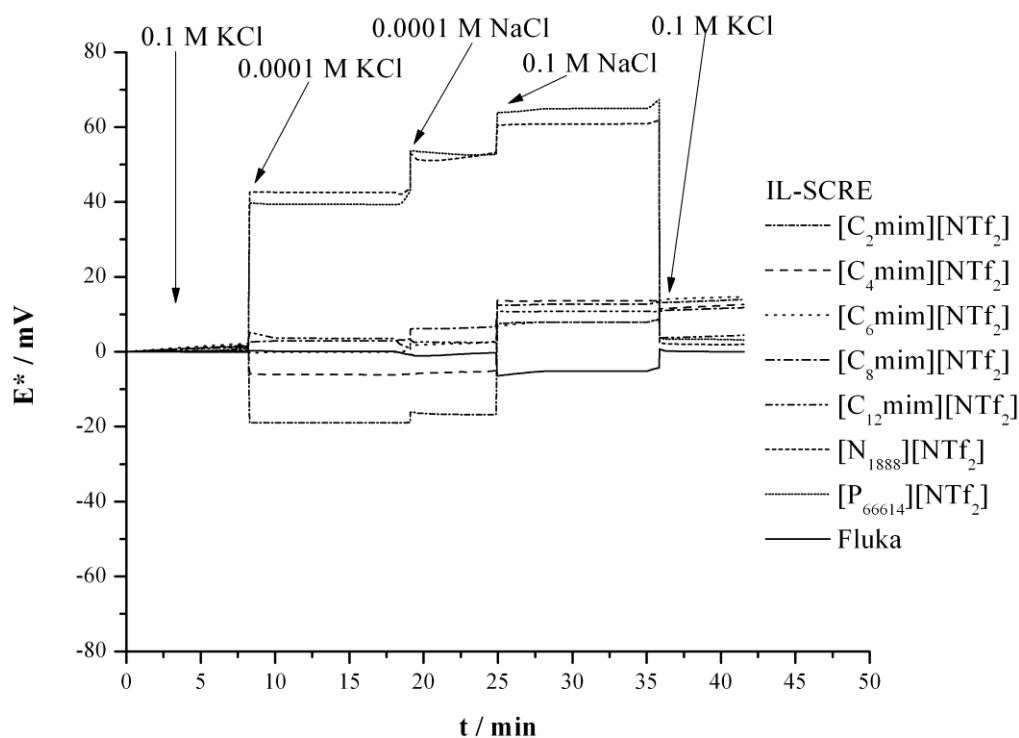


Figure 2. Potentiometric responses of membranes prepared on solid-contacts using PVC and ILs as listed on the figure. Membranes are exposed to electrolytes noted on the figure and signal is monitored over time. Note that all electrode responses were normalized at the response of Methrom RE obtained for initial exposure to 0.1M KCl. The scale at y-axis is kept to demonstrate the level of response of hereby-studied REs.

Phosphonium- and ammonium-based membranes showed large potential variations and were therefore unsuitable for further studies. According to Freire et al phosphonium-based ILs are very hygroscopic.[20] This is likely inducing ion exchange process of ions from the sample and IL and renders the membrane responsive to the sample ion, which is indicated as variation in the potential upon changing the sample. On the other hand, all $[C_n\text{mim}][\text{NTf}_2]$ SCREs showed excellent signal stability with $<15\text{mV}$ potential difference over three orders of magnitude of concentration change and $<10\text{mV}$ observed potential difference when changing the type of electrolyte at the highest used concentration (0.1M).

In order to confirm the hypothesis that the membrane potential depends only on $[C_n\text{mim}]^+$ (where n is the number of carbons in the chain) we prepared a PVC- $[C_2\text{mim}][\text{NTf}_2]$

membrane in a solid-contact electrode and used it as an indicator electrode against a classical Ag/AgCl reference electrode in the titration of series of salts. The indicator electrode was conditioned overnight in 10^{-3}M LiCl. Results are presented in Figure 3.

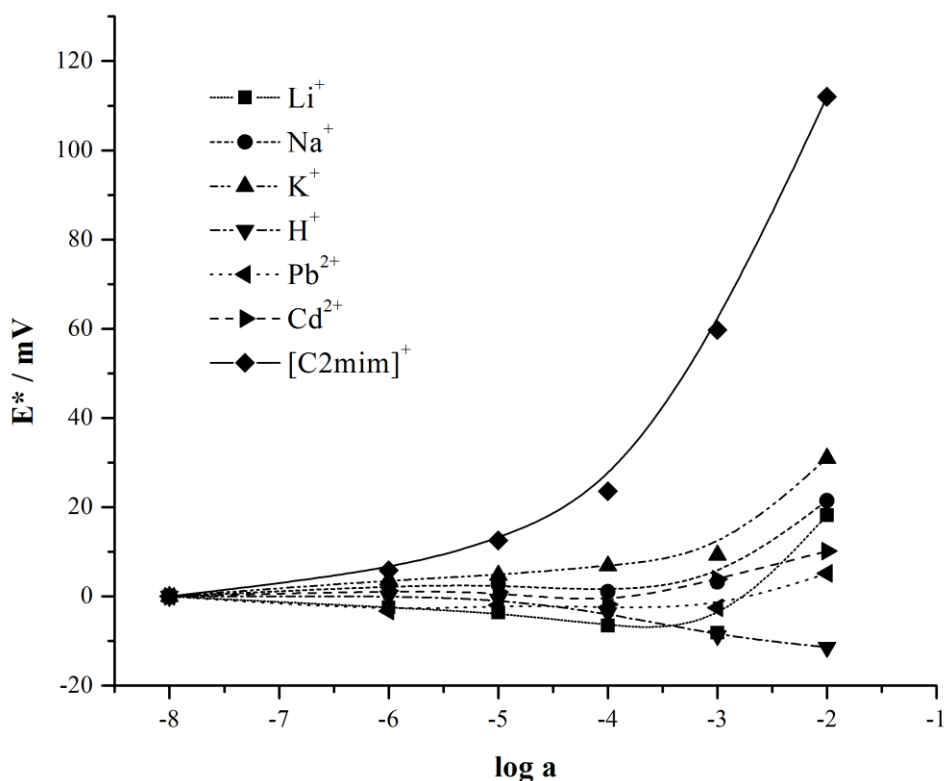


Figure 3. Potentiometric responses of solid-contact electrodes prepared using PVC and $[\text{C}_2\text{mim}][\text{NTf}_2]$ to a range of ions.

The potential change in every case was less than 10mV for concentrations less than 0.01M. The only exception was in the case of $[\text{C}_2\text{mim}]\text{Cl}$, with which a near-Nernstian response slope (52.4 mV/decade) towards $[\text{C}_2\text{mim}]^+$ ion was obtained. This indicates that this ion is responsible for defining the electrode response. Therefore, a membrane based on $[\text{C}_2\text{mim}][\text{NTf}_2]$ should be suitable for use as reference electrode according to Bakker's and Horvai's approaches [3].

In order to show insensitivity of the PVC-IL based RE to changes in electrolyte concentrations, while simultaneously to studying the speed and dynamics of the RE response, we have used protocols as described by Mattinen et al [7]. After preparation, the LCREs and SCREs were immersed in 0.1 M KCl and 0.01 M KCl for 10 min at a time, and rinsed with deionized water between solutions (Protocol I). The effect of larger concentration differences and changes in the mobility of the electrolyte ions were studied by immersing electrodes in 0.1 M KCl, 10^{-4} M KCl, 10^{-4} M NaCl, 0.1 M NaCl and 0.1 M KCl (Protocol II). The measurement time in each solution was 10 min, and electrodes were rinsed with deionized water between each measurement. The stabilization time of the electrodes was studied by moving the electrodes between 0.01M and 0.1M KCl every 30 seconds (Protocol III). The potential was measured against a commercial double junction Ag/AgCl electrode (Metrohm). Two commercially available reference electrodes were used as the working electrode in all measurements to confirm that the reference was working properly. They were a second Methrom Ag/AgCl double junction reference electrode and a commercially available solid-state reference electrode (REFEX Sensors Ltd). No stirring was applied to make the response diffusion controlled and to avoid convection effects. Results obtained using all three protocols on a SCRE are presented in Figure 4 from left to right respectively.

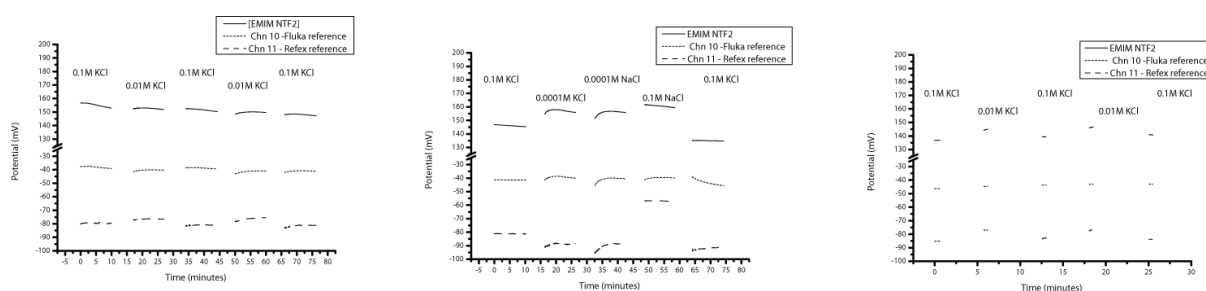


Figure 4. Potentiometric responses of [C₂mim][NTf₂]-based SCRE (full line) compared with responses of Methrom Ag/Ag/Cl (dashed line) and REFEX (dotted line) reference electrodes. Three protocols employed are described in the text. Responses using Protocol I are shown on the left, Protocol II in the middle and Protocol III on the right.

Protocol I (Figure 4 left) shows the potential differences caused by varying the concentration of the same electrolyte. In this case, the response of [C₂mim][NTf₂] electrode (blue lines) is almost identical to responses of other two commercial REs (Methrom – green line) and REFEX (red line). Figure 4 (middle) shows the influence of larger concentration differences and different mobilities of ions. In this case, the response of the Methrom RE (green line) is very stable, which is not surprising given the fact that two identical electrodes are coupled in the cell, one as RE and another as the indicator electrode. Interestingly, the REFEX RE (red line) shows some slight sensitivity towards Na⁺ ions, with potential increasing by ~30mV over three orders of magnitude change in Na⁺ concentration. On the other hand, [C₂mim][NTf₂] electrode (blue lines) demonstrated better stability towards large concentration changes with <15mV change in signal occurring for changes of over three orders of magnitude in concentration. Interestingly, ~25 mV potential difference is observed when changing the type of electrolyte at the highest concentration used (0.1M). Negligible potential difference is observed when the type of electrolyte was changed at lower concentrations (10⁻⁴M). The potential difference change at high concentration can most likely be attributed to different mobilities of Na⁺ and K⁺ ions. However, since the membrane is not very responsive to these ions, this influence is observed only at very high concentrations of these ions. Finally, the [C₂mim][NTf₂] electrode showed excellent dynamic response. (Figure 4 right) shows stable responses occurring within seconds of a change in the electrolyte.

It is important to note that we tested long term-stability by keeping membranes dry over periods of several weeks. Electrodes were first tested after one week by reconditioned overnight prior the use and testing their stability by using protocol I followed by calibration of the pH-selective electrode. We used at least 4 REs in these studies. After first day we obtained mean potential value of 69 mV with 2.2 mV as standard deviation. After storing

electrodes for three and ten days tests showed mean potential of 69.4 ± 2.3 mV and 71.3 ± 2.2 mV respectively.

Very often H^+ and OH^- ions can have a serious effect on both indicator and reference electrodes and it is therefore important to understand the influence of these ions on the $[C_2mim][NTf_2]$ RE. Figure 5 depicts the effect of pH on the response of $[C_2mim][NTf_2]$ electrode (black dots) and the two commercial REs used as indicators electrodes (Methrom – green diamonds and REFEX – blue triangles).

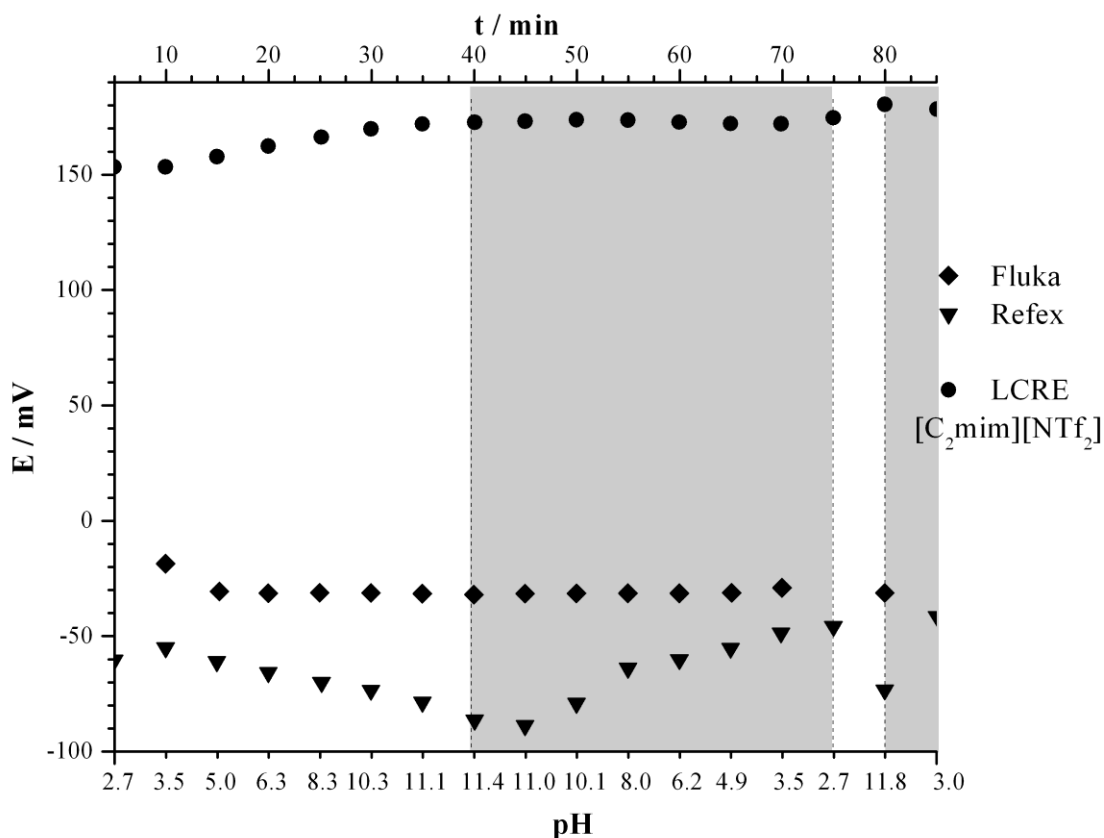


Figure 5. Potentiometric pH responses of $[C_2mim][NTf_2]$ -based SCRE (circles), Methrom (diamonds) and REFEX reference electrodes (triangles). The white region of the graph depicts the response to increasing pH, while shaded region depicts the response to decreasing pH. The far right of the graph shows the response to a sudden pH change from 2.7 to 11.8 (white portion) and then back to pH=3 (shaded region).

This experiment was performed with a universal buffer solution, using solutions of NaOH and HNO₃ to change the pH in cyclic manner from pH=2.7 to pH=11.4. Initially, the pH was changed in smaller increments, followed by large step changes between the two extreme pH values. The effect of increasing pH is shown in the unshaded region, while the effect of decreasing the pH decrease is shown in the shaded region of the Figure 5. Again, as expected, the Methrom RE did not show any noticeable potential change, as two identical electrodes are coupled as the indicator and reference electrode in this experiment. The REFEX electrode gave a potential difference of >40mV for the entire studied pH range. Interestingly, [C₂mim][NTf₂] electrode again shows somewhat better performance than REFEX. The potential difference over the entire pH range was initially >20mV. This difference disappeared in the second cycle of pH change (shaded region) and was almost unnoticeable during the extreme changes of pH.

Application

Initial characterization showed that membrane based on [C₂mim][NTf₂] has excellent potential to be utilized as reference electrode. The following section focuses on the performance of this SCRE in various electrochemical techniques.

Potentiometry

The [C₂mim][NTf₂]-based RE was used to produce calibration curves of Pb²⁺- and pH-selective electrodes, and these were compared to response curves of same ISEs coupled with a classical Ag/AgCl RE. After conditioning (see experimental) the Pb²⁺-selective electrodes were immersed in a pH=3.0 solution while the pH-selective electrodes were immersed in a solution of universal buffer. Response curves of the Pb²⁺-selective electrodes were recorded by monitoring the potential upon addition of aliquots of Pb(NO₃)₂, while the response of pH-selective electrodes was by changing the pH using solutions of NaOH and HNO₃. Figure 6

left depicts the results obtained with the Pb^{2+} -selective electrode versus the $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based SCRE (circles), and the same ISE coupled with the Methrom RE (squares). Figure 6 (right) depicts results obtained with the pH-selective electrode versus the $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based SCRE (circles), and the same pH electrode coupled with the Methrom RE (squares).

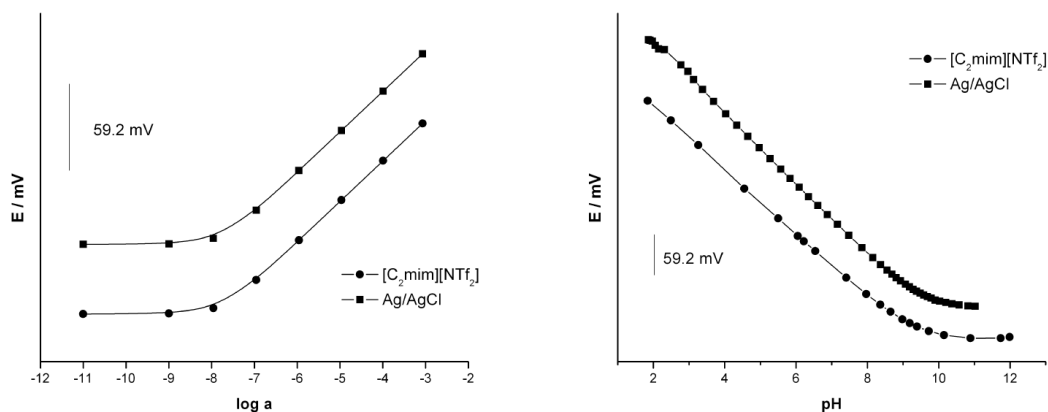


Figure 6. Left) Response of the SC Pb^{2+} -selective electrode coupled with $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based SCRE (circles) and Methrom Ag/AgCl RE (squares). The slopes are 28.1 mV/decade and 26.5 mV/decade, respectively. The detection limit of $2 \times 10^{-8} \text{M}$ is identical for both electrodes. Right) Response of the SC pH-selective electrode coupled with $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based SCRE (circles) and Methrom Ag/AgCl RE (squares). The slopes are 55.4 mV/decade and 51.2 mV/decade, respectively.

The most striking feature of both parts of Figure 6 is that the responses of the ISEs coupled with the Fluke RE are almost identical to their responses when coupled with the $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based SCRE. The Pb^{2+} -selective electrode has a slope of 28.1 mV/decade and 26.5 vs the Methrom and the $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based SCRE, respectively. The detection limits are identical at $2 \times 10^{-8} \text{M}$, which corresponds closely to the theoretically predicted detection limit of $1.6 \times 10^{-8} \text{M}$ [21]. The slopes of pH-selective electrodes were 55.4 mV/decade and 51.2 vs the Methrom and the $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based SCRE, respectively. The linear ranges spanned from $\text{pH}=2$ to $\text{pH}=10.1$ versus the Methrom RE, and from $\text{pH}=2$ to $\text{pH}=10.2$ versus the $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based SCRE.

Cyclic Voltammetry

In order to test the potential of [C₂mim][NTf₂]-based RE in voltammetry, we compared the reduction/oxidation of the Fe^{III}(CN)₆³⁻/Fe^{II}(CN)₆⁴⁻ redox couple on a Pt electrode versus the Methrom and the [C₂mim][NTf₂]-based SCRE. The resulting voltammograms (Figure 7) are almost identical. The voltammogram obtained using the Methrom RE is shown with a full line while three obtained with different [C₂mim][NTf₂]-based SCREs are shown using dashed lines. The latter emphasises the excellent reproducibility of the voltammograms obtained with three different SCREs. The different position on the potential axes of the voltammograms obtained using different REs is a consequence of the different reference potential for each RE. However, the similarity in key parameters such as the difference in cathodic and anodic maxima is virtually identical, to within the margin of error of the measurement (0.135±0.005V) which once again reinforces the usefulness of the SCRE

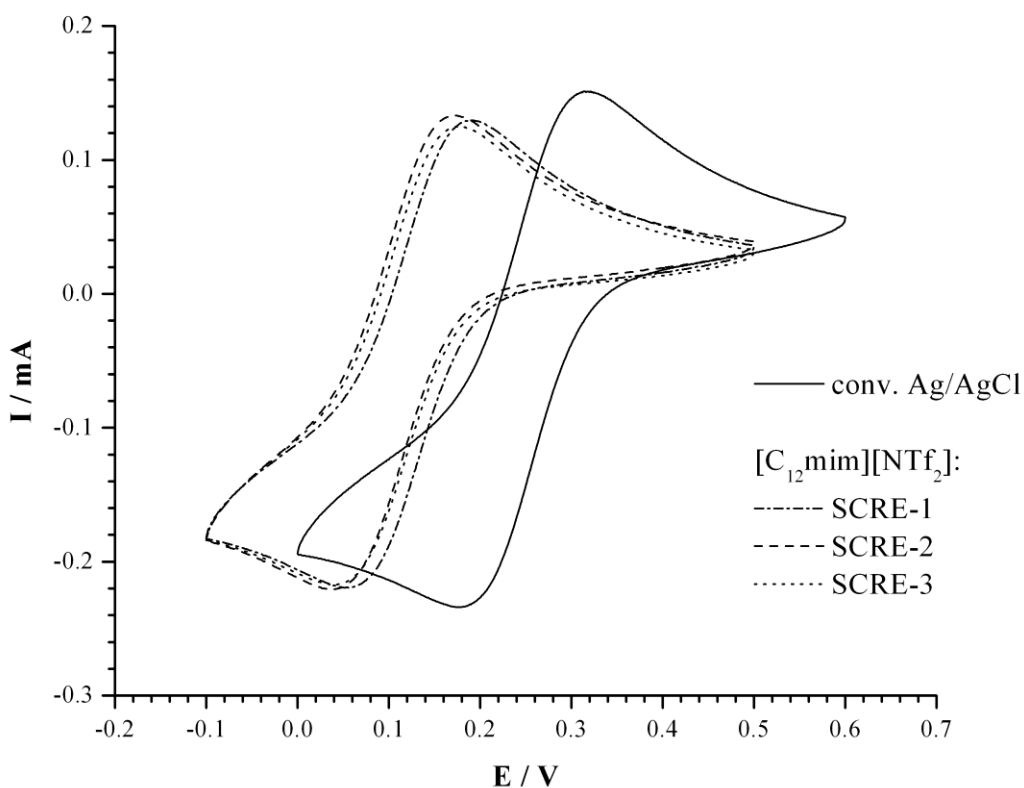


Figure 7. Cyclic voltammogram of $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}/\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ redox couple at a Pt electrode versus Methrom (full line) and three different $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based REs.

Impedance spectroscopy

The applicability of the $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based SCRE to Electrochemical Impedance Spectroscopy (EIS) was tested by comparing spectra obtained with the PVC-[P4,4,4,14][NTf2] membrane recorded against the Ag/AgCl electrode and $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based SCRE. Figure 8 compares the resulting spectra. By fitting of the curve using the equivalent circuits presented in the inset (Figure 8), $R_1=5400\Omega$ and $Q=1\times 10^{-7}$ were obtained using $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based SCRE while values of $R_1=5500\Omega$ and $Q=1\times 10^{-7}$ were obtained with Methrom RE. Excellent correspondence confirms the applicability of the $[\text{C}_2\text{mim}][\text{NTf}_2]$ -based SCRE for EIS measurements.

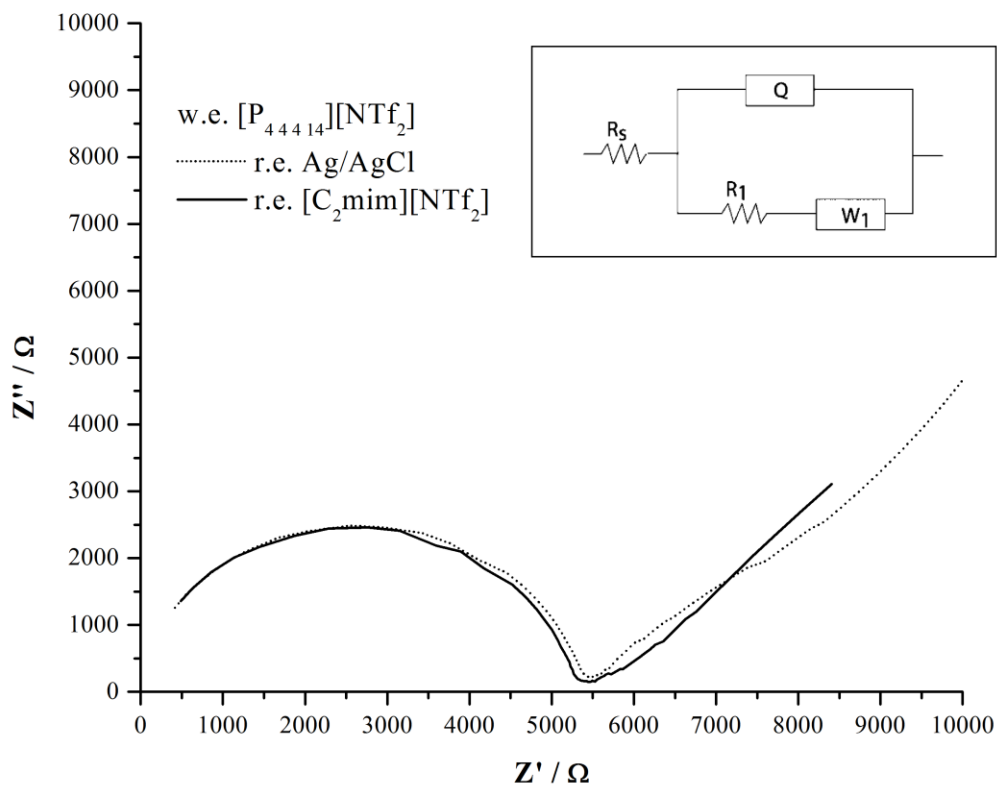


Figure 8. Nyquist plots of PVC-[P4,4,4,14][NTf₂] membrane recorded versus Ag/AgCl electrode (dotted line) and versus [C₂mim][NTf₂]-based SCRE (full line). The inset illustrates the equivalent circuit used to fit the experimental data; where R_s and R_1 are solution and membrane resistance, respectively, Q is constant phase element and W is Warburg impedance. Frequency range was 0.01-10000Hz.

Conclusions

We have developed a very simple polymer membrane that can be used to make very effective solid-contact reference electrodes (SCREs). The membrane is prepared using only polymer (PVC) and an ionic liquid (IL) as the plasticizer. The IL contains ions that are partially soluble in water, which enables them to form a stable membrane boundary potential. The

performance of the SCREs was compared against two commercially available REs in the range of electrochemical techniques. The [C₂mim][NTf₂]-based SCREs in particular showed excellent stability and electrodes were successfully used in the potentiometric titration of Pb²⁺ and pH. Calibration plots returned Nernstian slopes with almost identical limits of detection. Cyclic voltammograms of Fe^{III}(CN)₆³⁻/Fe^{II}(CN)₆⁴⁻ on a Pt electrode were also almost identical, albeit offset due to the different reference potential of the reference electrodes. Finally, excellent correspondence in EIS spectra using the two REs indicates that [C₂mim][NTf₂] can be successfully used in EIS in addition to potentiometry and cyclic voltammetry.

Moreover, we prepared both LCRE and SCRE and both types of REs behaved almost identically. Both SCREs and SC-ISEs were prepared in the same fashion – the only differences were in formulation of the PCV capping membrane. Due to the simplicity and possibility for mass-production, these SCREs have excellent potential for coupling with similarly fabricated SC-ISEs to produce extremely low-cost yet very sensitive chemical sensors.

Acknowledgments

This research was supported by Science Foundation Ireland (CLARITY, Centre for Sensor Web Technologies, award no. 07/CE/I1147 and NAP210), and by the EU MATERA Programme (Enterprise Ireland MASTRA - TD/2006/0341). AR also thanks DCU for a Research Fellowship and Research Career Start Award and the University of Portsmouth for Starting Lecturer Fund. DC is thankful for a CLARITY-MASTRA internship.

Literature

- [1] R. W. Murray, *Anal. Chem.* 2010, 82, 1569-1569.
- [2] C. Fay, S. Anastasova, C. Slater, S. T. Buda, R. Shepherd, B. Corcoran, N. O'Connor, G. Wallace, A. Radu and D. Diamond, *IEEE Sens. J.* accepted.
- [3] E. Bakker, *Electroanalysis* 1999, 11, 788-792.
- [4] D. Diamond, E. McEnroe, M. McCarrick and A. Lewenstam, *Electroanalysis* 1994, 6, 962-971.
- [5] A. Kisiel, H. Marcisz, A. Michalska and K. Maksymiuk, *Analyst* 2005, 130, 1655-1662.
- [6] A. Kisiel, A. Michalska, K. Maksymiuk and E. A. H. Hall, *Electroanalysis* 2008, 20, 318-323.
- [7] U. Mattinen, J. Bobacka and A. Lewenstam, *Electroanalysis* 2009, 21, 1955-1960.
- [8] S. Anastasova-Ivanova, U. Mattinen, A. Radu, J. Bobacka, A. Lewenstam, J. Migdalski, M. Danielewski and D. Diamond, *Sensors Act B* 2010, 146, 199-205.
- [9] A. Vincze and G. Horvai in Vol. 97-19 Eds.: A. J. Ricco, M. A. Butler, P. Vanysec, G. Horvai and A. F. Silva), *Sensor and Physical Electrochemistry Divisions*, Pennington, NJ, 1997, pp. 550-555.
- [10] Y. M. Mi, S. Mathison and E. Bakker, *Electrochemical and Solid State Letters* 1999, 2, 198-200.
- [11] T. Blaz, J. Migdalski and A. Lewenstam, *Analyst* 2005, 130, 637-643.
- [12] T. Kakiuchi, T. Yoshimatsu and N. Nishi, *Anal. Chem.* 2007, 79, 7187-7191.
- [13] T. Yoshimatsu and T. Kakiuchi, *Anal. Sci.* 2007, 23, 1049-1052.
- [14] D. V. Chernyshov, M. G. Khrenova, I. V. Pletnev and N. V. Shvedene, *Mendeleev Commun.* 2008, 18, 88-89.
- [15] N. Nishi, H. Murakami, Y. Yasui and T. Kakiuchi, *Anal. Sci.* 2008, 24, 1315-1320.
- [16] B. Peng, J. W. Zhu, X. J. Liu and Y. Qin, *Sensors Act B* 2008, 133, 308-314.
- [17] N. V. Shvedene, D. V. Chernyshov, M. G. Khrenova, A. A. Formanovsky, V. E. Baulin and I. V. Pletnev, *Electroanalysis* 2006, 18, 1416-1421.
- [18] A. Marciniak, *Inter. J. Molecular Sci.* 2010, 11, 1973-1990.
- [19] T. Kakiuchi, *Anal. Sci.* 2008, 24, 1221-1230.
- [20] M. G. Freire, P. J. Carvalho, R. L. Gardas, L. M. N. B. F. Santos, I. M. Marrucho and J. A. P. Coutinho, *J. Chem. Eng. Data* 2008, 10, 2378-2382.
- [21] A. Radu, S. Peper, E. Bakker and D. Diamond, *Electroanalysis* 2007, 19, 144-154.