

Petter Danielsson · Johan Bobacka · Ari Ivaska

## Electrochemical synthesis and characterization of poly(3,4-ethylenedioxythiophene) in ionic liquids with bulky organic anions

Published online: 12 August 2004  
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**Abstract** The electrochemistry of poly(3,4-ethylenedioxythiophene) (PEDOT) was studied in two ionic liquids with bulky organic anions, i.e., 1-butyl-3-methylimidazolium (BMIM) diethylene glycol monomethyl ether sulfate (MDEGSO<sub>4</sub>) and BMIM octyl sulfate (OctSO<sub>4</sub>). BMIM-MDEGSO<sub>4</sub> is a liquid, while BMIM-OctSO<sub>4</sub> is in solid form at room temperature. Electrosynthesis of PEDOT in BMIM-MDEGSO<sub>4</sub> with an EDOT concentration of 0.1 M and in BMIM-MDEGSO<sub>4</sub>/EDOT 1/1 (w/w) solution resulted in no polymer at all or a very limited amount of polymer on the electrode surface, as determined by cyclic voltammetry in 0.1 M KCl(aq) solution. In contrast, electrosynthesis of PEDOT in BMIM-OctSO<sub>4</sub>/EDOT 1/1 (w/w) resulted in a high yield of electroactive material on the electrode surface. Furthermore, electrosynthesis of PEDOT in ionic liquid–water solution ( $C_{\text{ionic liquid}} = 1.5$  M) containing 0.1 M EDOT was also found to give a relatively high yield of electroactive material on the electrode surface, both for 1.5 M BMIM-MDEGSO<sub>4</sub>(aq) and 1.5 M BMIM-OctSO<sub>4</sub>(aq). The PEDOT electrodes showed an anionic potentiometric response in  $10^{-5}$ – $10^{-1}$  M KCl(aq) solution, indicating a predominant anion transfer at the polymer–solution interface despite the relatively bulky anions (MDEGSO<sub>4</sub><sup>−</sup> or OctSO<sub>4</sub><sup>−</sup>) incorporated as counterions in PEDOT during electropolymerization. On the basis of electrochemical impedance spectroscopy, the charge (ion) transport properties of the polymer film were strongly influenced by the water content of the ionic liquid ( $C_{\text{ionic liquid}} = 0.05$ – $2.0$  M).

**Keywords** Conducting polymer · Ionic liquid · Cyclic voltammetry · Potentiometry · Electrochemical impedance spectroscopy

### Introduction

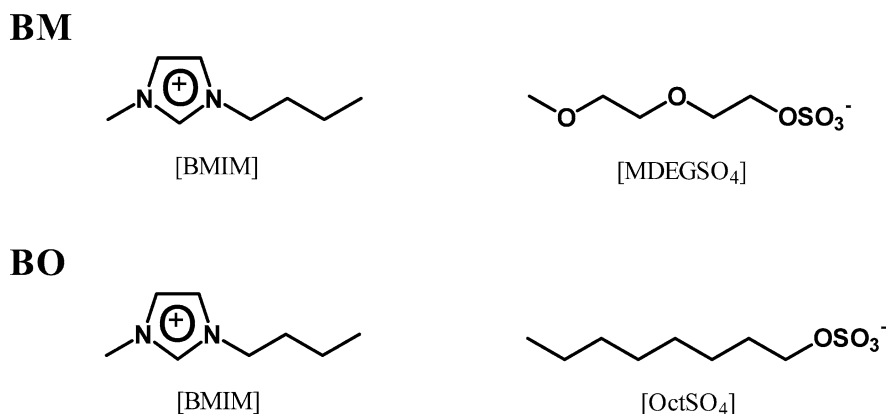
Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the stablest conducting polymers available today [1, 2]. The polymer can be electrosynthesized from the monomer in both aqueous and organic solutions in the presence of a suitable electrolyte salt [3, 4]. Recently, some ionic liquids, such as 1-ethyl-3-methyl-1-*H*-imidazolium bis(trifluoromethanesulfonyl)imide, 1-butyl-3-methylimidazolium (BMIM) chloride, BMIM tetrafluoroborate and BMIM hexafluorophosphate, were used as electrolyte solution in the electrosynthesis of PEDOT [5, 6]. Compared with ordinary solvents, which consist of molecules, ionic liquids consist of negatively and positively charged ions. By combining different cations with different anions, a trillion ionic liquids are theoretically possible [7]. Ionic liquids are not a new discovery and the ionic liquid ethyl ammonium nitrate was mentioned in the literature as long ago as 1914 [8]. However, recently ionic liquids have attracted much interest because of their unique chemical and physical properties. They are nonvolatile, nonflammable, have low toxicity and high thermal stability and are good solvents for a wide range of organic and inorganic materials. Because of these properties, ionic liquids have been proposed as replacements for volatile organic compounds in chemical processes and extractions [9, 10, 11]. Furthermore, ionic liquids often have wide electrochemical windows, and good electrical conductivity and solvent transport properties, which make them desirable as electrochemical solvents [12].

BMIM diethylene glycol monomethyl ether sulfate (MDEGSO<sub>4</sub>) and BMIM octyl sulfate (OctSO<sub>4</sub>) are ionic liquids consisting of relatively bulky cations and anions, as shown in Fig. 1. In the present work,

Dedicated to Zbigniew Galus on the occasion of his 70th birthday

P. Danielsson · J. Bobacka (✉) · A. Ivaska  
Process Chemistry Group,  
c/o Laboratory of Analytical Chemistry,  
Åbo Akademi University, Biskopsgatan 8,  
20500 Åbo-Turku, Finland  
E-mail: johan.bobacka@abo.fi  
Tel.: +358-2-2153246  
Fax: +358-2-2154479

**Fig. 1** Chemical structure of the two ionic liquids used: 1-butyl-3-methylimidazolium (*BMIM*) diethylene glycol monomethyl ether sulfate (*MDEGSO<sub>4</sub>*) (*BM*), *BMIM* octyl sulfate (*OctSO<sub>4</sub>*) (*BO*)



BMIM-MDEGSO<sub>4</sub> and BMIM-OctSO<sub>4</sub> with different amounts of water were studied as electrolyte solutions in the electrosynthesis and electrochemical characterization of PEDOT by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Since the potentiometric response of conducting polymer-based electrodes may vary from anionic to cationic depending on the mobility of the doping anions [13], the potentiometric response of PEDOT doped with MDEGSO<sub>4</sub><sup>-</sup> and OctSO<sub>4</sub><sup>-</sup> was studied as well.

## Experimental

### Chemicals

The monomer, 3,4 ethylenedioxythiophene (EDOT, more than 97%), was obtained from Bayer. The ionic liquids, BMIM-MDEGSO<sub>4</sub> (more than 98%) and BMIM-OctSO<sub>4</sub> (more than 98%), were obtained from Solvent Innovation. BMIM-MDEGSO<sub>4</sub> and BMIM-OctSO<sub>4</sub> will be referred to as BM and BO, respectively. Distilled, deionized water was used in the solution preparations.

### Electrochemical cell

The electrochemical polymerization, CV and electrochemical impedance measurements were performed in a three-electrode cell. The working electrode was a glassy carbon (GC) disk electrode (area 0.07 cm<sup>2</sup>) and a GC-rod was used as a counter electrode. A silver wire was used as pseudoreference electrode. Prior to the measurements the solutions were purged with nitrogen, and the measurements were performed under a nitrogen atmosphere at room temperature (23 ± 2 °C).

### Electropolymerization

PEDOT was electrosynthesized by galvanostatic electropolymerization of EDOT on GC by using the ionic liquids BM and BO as electrolytes. BM is a liquid at room temperature and the electropolymerizations were performed in the following three solutions:

- 1a. BM (water-free solution) with an EDOT concentration of 0.1 M (BM plus 0.1 M EDOT).
- 1b. BM/EDOT 1/1 (w/w) solution ( $C_{\text{EDOT}} \sim 4.7$  M) (BM/EDOT 1/1).
- 1c. BM/water solution, where the concentration of BM was approximately 1.5 M and the concentration of EDOT was 0.1 M [1.5 M BM(aq) plus 0.1 M EDOT].

The mixture of BM and EDOT (1b) as well as that of BM and water (1c) resulted after stirring in one phase, indicating that both EDOT and water are completely miscible with BM.

BO has a melting point of 33 °C and is therefore a solid at room temperature. Therefore the polymerization in BM plus 0.1 M EDOT (hypothetical solution 2a) was not studied. However, BO was found to be soluble in both EDOT and water, so the following two BO solutions were used:

- 2b. BO/EDOT 1/1 (w/w) solution ( $C_{\text{EDOT}} \sim 4.7$  M) (BO/EDOT 1/1).
- 2c. BO/water solution, where the concentration of BO was approximately 1.5 M and the EDOT concentration was 0.1 M [1.5 M BO(aq) plus 0.1 M EDOT].

Prior to all the polymerizations the GC working electrode was polished with 0.3- $\mu\text{m}$  alumina and rinsed with deionized water. The galvanostatic polymerization was performed at a current of 0.014 mA (0.2 mA/cm<sup>2</sup>) that was applied for 714 s. For comparison, potentiodynamic polymerization was also performed in solutions 1c and 2c. The potential range was -0.5 to 1.2 V for solution 1c and -0.5 to 0.9 V for solution 2c. The scan rate was 50 mV/s and a total number of 20 scans were performed.

### Cyclic voltammetry

After polymerization the GC/PEDOT(BM) and GC/PEDOT(BO) electrodes were studied by CV in a 0.1 M KCl(aq) solution. The potential range was -0.5 to 0.5 V and the scan rate was 100 mV/s. The GC/PEDOT(BM) and GC/PEDOT(BO) electrodes were also studied by

CV in different concentrations of BM(aq) and BO(aq), respectively.

### Electrochemical impedance spectroscopy

EIS was performed by using an Autolab frequency response analyzer system (AUT20.FRA-AUTOLAB, ECO Chemie, The Netherlands). The impedance spectra were recorded in the frequency range 100 kHz–10 mHz by using a sinusoidal excitation signal with an amplitude of 10 mV. The measurements were performed in BM(aq) solutions of different concentrations (from 0.05 M to pure BM, which is about 3.8 M) and in BO(aq) solutions of different concentrations (0.05–2.0 M) at an  $E_{dc}$  value of 0.2 V. The impedance spectra were fitted to an equivalent electrical circuit by using the Autolab impedance analysis software.

### Potentiometric measurements

Potentiometric measurements were performed at room temperature ( $23 \pm 2$  °C) with a homemade multichannel millivolt meter connected to a PC for data acquisition. The potentiometric responses for GC/PEDOT(BM) and GC/PEDOT(BO) electrodes were obtained in KCl(aq), BM(aq) and BO(aq) solutions in the concentration range  $10^{-1}$ – $10^{-5}$  M. The reference electrode in the potentiometric measurements was an Ag/AgCl/KCl (3 M) electrode.

## Results and Discussion

### Electrochemical polymerization in ionic liquid–EDOT solutions

The chronopotentiometric curve recorded during the galvanostatic electropolymerization of EDOT (0.1 M) in pure BM (solution 1a) is shown in Fig. 2 (curve 1). During the polymerization the potential rises to about 1.3 V (versus Ag wire) and increases slightly with time. The cyclic voltammogram of the resulting GC/PEDOT(BM) electrode in 0.1 M KCl(aq) shows a similar current as a the bare GC electrode (Fig. 3a, curves 1, 2), indicating that practically no polymer film was formed on the electrode during the polymerization in solution 1a. The chronopotentiometric curve, obtained during the electropolymerization in BM/EDOT 1/1 (Fig. 2, curve 2) is very similar to that obtained in solution 1a (Fig. 2, curve 1). However, the subsequent cyclic voltammogram of the GC/PEDOT(BM) electrode (Fig. 3a, curve 3) shows that some polymer was formed on the electrode from solution 1b. This shows that the increase of the EDOT concentration from 0.1 M to about 4.6 M facilitated the polymerization only slightly. In contrast, in BO/EDOT 1/1 (solution 2b) the polymerization takes place at a significantly lower potential

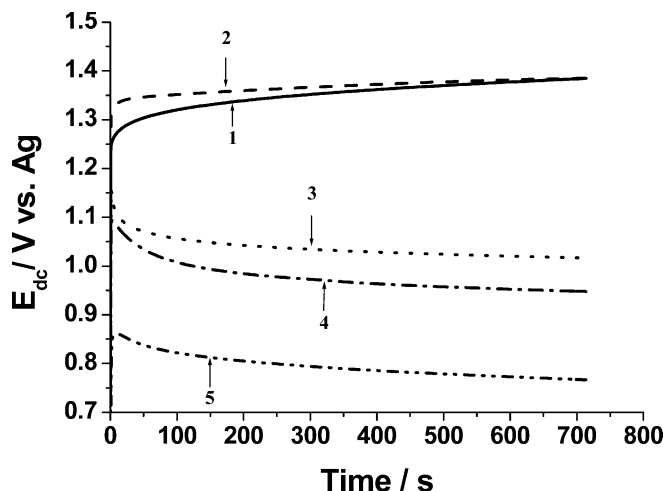
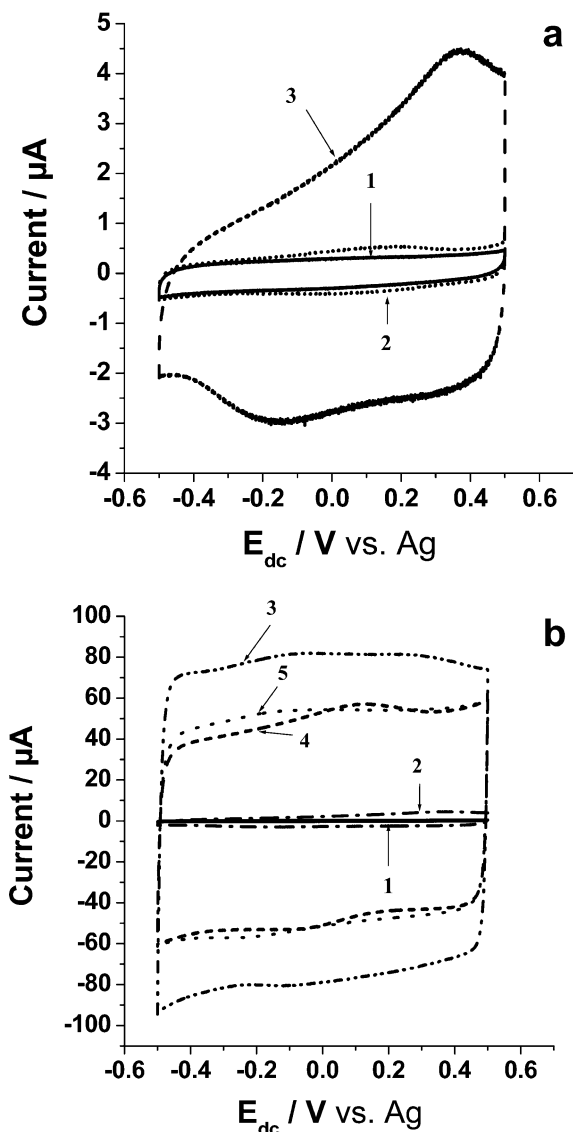


Fig. 2 Chronopotentiometric curves obtained during galvanostatic polymerization of 3,4-ethylenedioxythiophene (EDOT) in BM plus 0.1 M EDOT (1), BM/EDOT 1/1 (w/w) (2), BO/EDOT 1/1 (w/w) (3), 1.5 M BM(aq) plus 0.1 M EDOT (4) and 1.5 M BO(aq) plus 0.1 M EDOT (5). Current density  $0.2 \text{ mA/cm}^2$

of about 1.0–1.1 V (Fig. 2, curve 3) and the cyclic voltammogram of GC/PEDOT(BO) shows a larger current response (Fig. 3b, curve 3) than that of GC/PEDOT(BM) (Fig. 3b, curve 2). These results show that the two anions  $\text{MDEGSO}_4^-$  and  $\text{OctSO}_4^-$  strongly influence the electropolymerization of EDOT in pure ionic liquid–monomer solutions. On the basis of the CV curves in Fig. 3b, one can conclude that PEDOT polymerized in BO/EDOT 1/1 (solution 2b) shows a slightly higher electroactivity than PEDOT polymerized under the same conditions from an aqueous solution, such as 0.01 M EDOT plus 0.1 M sodium poly(styrene sulfonate) [14].

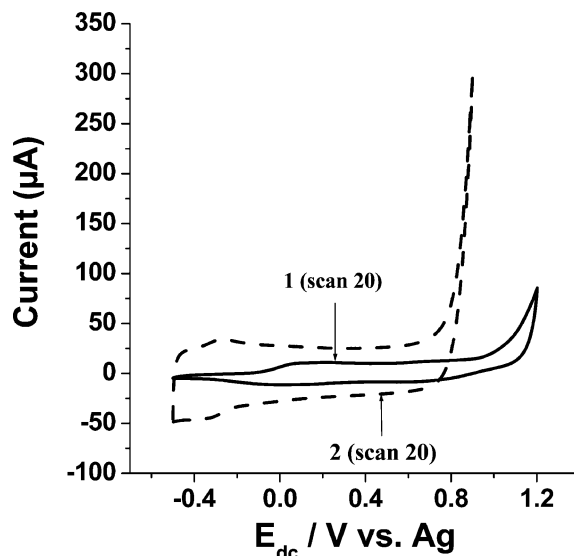
### Electrochemical polymerization in ionic liquid–water–EDOT solutions

As mentioned earlier, both BM and BO are miscible with water, resulting in one-phase solutions after stirring. Interestingly, electropolymerization of EDOT in 1.5 M BM(aq) plus 0.1 M EDOT (solution 1c) results in a relatively high yield of polymer on the electrode, as judged by CV (Fig. 3b, curve 4). Electropolymerization of EDOT in 1.5 M BO (aq) plus 0.1 M EDOT (solution 2c) results in the same yield of electroactive polymer, as judged by CV (Fig. 3b, curve 5). As shown in Fig. 2 (curves 4, 5), the electropolymerization occurs at a lower potential in 1.5 M BO(aq) than in 1.5 M BM(aq), indicating once more that the  $\text{OctSO}_4^-$  anion facilitates the polymerization of EDOT compared with the  $\text{MDEGSO}_4^-$  anion. This conclusion is supported by results from the potentiodynamic polymerization in the same solutions, 1c and 2c, as shown in Fig. 4. Polymerization of EDOT starts at a potential about 0.2 V lower in 1.5 M BO(aq) plus 0.1 M EDOT (solution 2c)



**Fig. 3a,b** Cyclic voltammograms recorded at a scan rate of 100 mV/s in 0.1 M KCl(aq) for different electrodes. **a** Bare glassy carbon (GC) electrode (1), GC/poly(EDOT) (PEDOT)(BM) electrode polymerized in BM plus 0.1 M EDOT (2) and GC/PEDOT(BM) electrode polymerized in BM/EDOT 1/1 (w/w) (3); scan rate 100 mV/s. **b** Bare GC electrode (1), GC/PEDOT(BM) electrode polymerized in BM/EDOT 1/1 (w/w) (2), GC/PEDOT(BO) electrode polymerized in BO/EDOT 1/1 (w/w) (3), GC/PEDOT(BM) electrode polymerized in 1.5 M BM(aq) plus 0.1 M EDOT (4) and GC/PEDOT(BO) polymerized in 1.5 M BO(aq) plus 0.1 M EDOT (5)

than in 1.5 M BM(aq) plus 0.1 M EDOT (solution 1c). Earlier studies showed that anionic surfactants like sodium dodecyl sulfate lower the oxidation potential of EDOT in aqueous solutions [15, 16]. Analogously, the  $\text{OctSO}_4^-$  anion has a hydrophobic (nonpolar) octyl chain and a hydrophilic (polar) sulfate group, which are expected to make it amphiphilic. This may be the reason why the polymerization of EDOT takes place at a lower potential in 1.5 M BO(aq) than in 1.5 M BM(aq). The surfactant properties of  $\text{OctSO}_4^-$  may thus be the reason



**Fig. 4** Potentiodynamic polymerization of EDOT in 1.5 M BM(aq) plus 0.1 M EDOT (1) and 1.5 M BO(aq) plus 0.1 M EDOT (2). Scan rate 50 mV/s. Scan number 20 is shown

for the higher yield of PEDOT also in water-free solution as discussed earlier (Fig. 3).

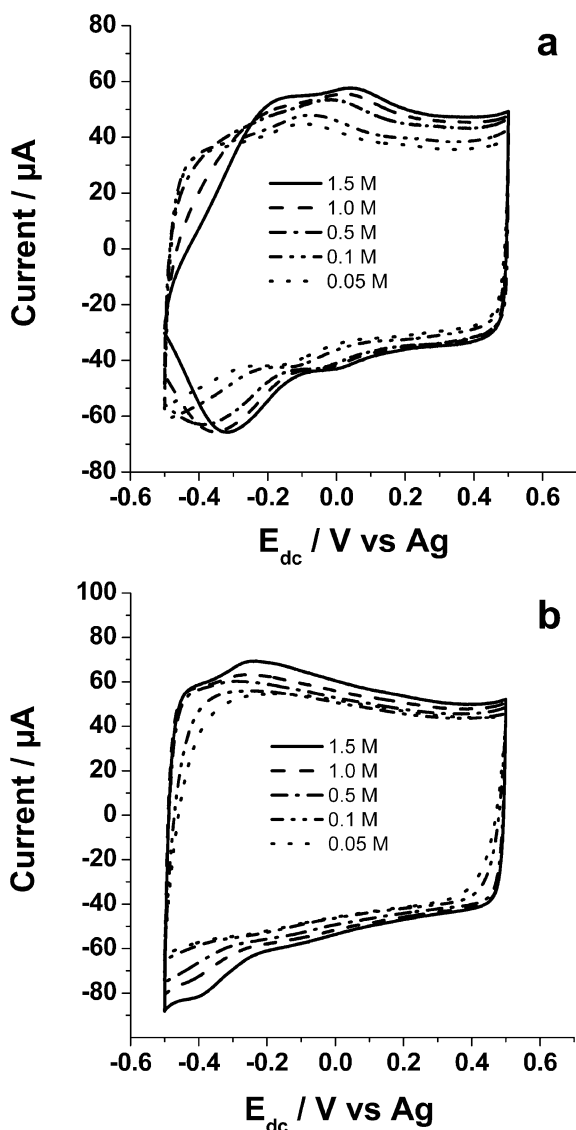
The CV curves recorded after the galvanostatic polymerizations show that the yield of electroactive PEDOT is about the same in solutions 1c and 2c (Fig. 3b, curves 4, 5). However, CV also shows that BO/EDOT 1/1 (solution 2b) gives a higher polymer yield than solution 2c (Fig. 3b, curves 3, 5) although the polymerization potential is about 0.2 V higher for solution 2b than for solution 2c (Fig. 2, curves 3, 5). These results indicate that the addition of water to BO lowers the polymerization potential and results in a lower yield of electroactive polymer on the electrode surface. In contrast, for BM a very small amount of polymer was formed in water-free solution (Fig. 3).

### Cyclic voltammetry

The PEDOT films polymerized in 1.5 M BM(aq) and 1.5 M BO(aq) solutions were investigated in monomer free BM(aq) and BO(aq) solutions of different concentrations (0.05–1.5 M). The GC/PEDOT(BM) electrodes were investigated in BM(aq) solutions and the GC/PEDOT(BO) electrodes in BO(aq) solutions. The potential range was  $-0.5$  to  $0.5$  V versus Ag wire and the scan rate was 100 mV/s. As can be seen in Fig. 5, the GC/PEDOT electrodes are electroactive in both BM(aq) and BO(aq) solutions. The  $Q_{\text{CV}}$  values were calculated for the GC/PEDOT(BO) and the GC/PEDOT(BM) electrodes and were obtained by integration of the cyclic voltammograms in the potential range  $-0.5$  to  $0.5$  V as follows:

$$Q_{\text{CV}} = (Q_{\text{a}} + Q_{\text{c}})/2, \quad (1)$$

where  $Q_{\text{a}}$  is the anodic charge and  $Q_{\text{c}}$  is the cathodic charge. The  $Q_{\text{CV}}$  values for the electrodes are shown in



**Fig. 5** Cyclic voltammograms of **a** GC/PEDOT(BM) in BM(aq) solutions and **b** GC/PEDOT(BO) in BO(aq) solutions of different concentrations. Scan rate 100 mV/s

Table 1. The cyclic voltammograms of the GC/PEDOT(BO) electrodes do not show any clear oxidation or reduction peaks in this potential range. As seen in

**Table 1**  $Q_{CV}$  values of glassy carbon (GC)/poly(3,4-ethylenedioxythiophene) (PEDOT)(1-butyl-3-methylimidazolium diethylene glycol monomethyl ether sulfate) (BM) and GC/PEDOT(1-butyl-3-methylimidazolium octyl sulfate) (BO) in BM(aq) and BO(aq) solutions, respectively.  $Q_a$  is the anodic charge and  $Q_c$  is the cathodic charge.  $Q_{CV} = (Q_a + Q_c)/2$

$C_{\text{ionic liquid}}/M$	GC/PEDOT(BM)			GC/PEDOT(BO)		
	$Q_a/\mu C$	$Q_c/\mu C$	$Q_{CV}/\mu C$	$Q_a/\mu C$	$Q_c/\mu C$	$Q_{CV}/\mu C$
0.05	365	362	363	476	472	474
0.1	388	385	386	484	478	481
0.5	425	426	425	521	517	519
1	424	433	429	553	546	550
1.5	422	433	427	590	588	589

Table 1 the charges ( $Q_{CV}$ ) decrease with decreasing concentrations of BO. For the GC/PEDOT(BM) redox peaks can be observed in the voltammograms performed in the solutions of the highest BM concentrations (0.5–1.5 M); however, the redox peaks cannot be observed in voltammograms performed in the solutions of the lowest concentrations (0.05 and 0.1 M). The results indicate that the doping of PEDOT(BM) is facilitated with increasing water concentration in BM(aq). As already shown, water also facilitated the electropolymerization of EDOT in BM solution.

### Potentiometry

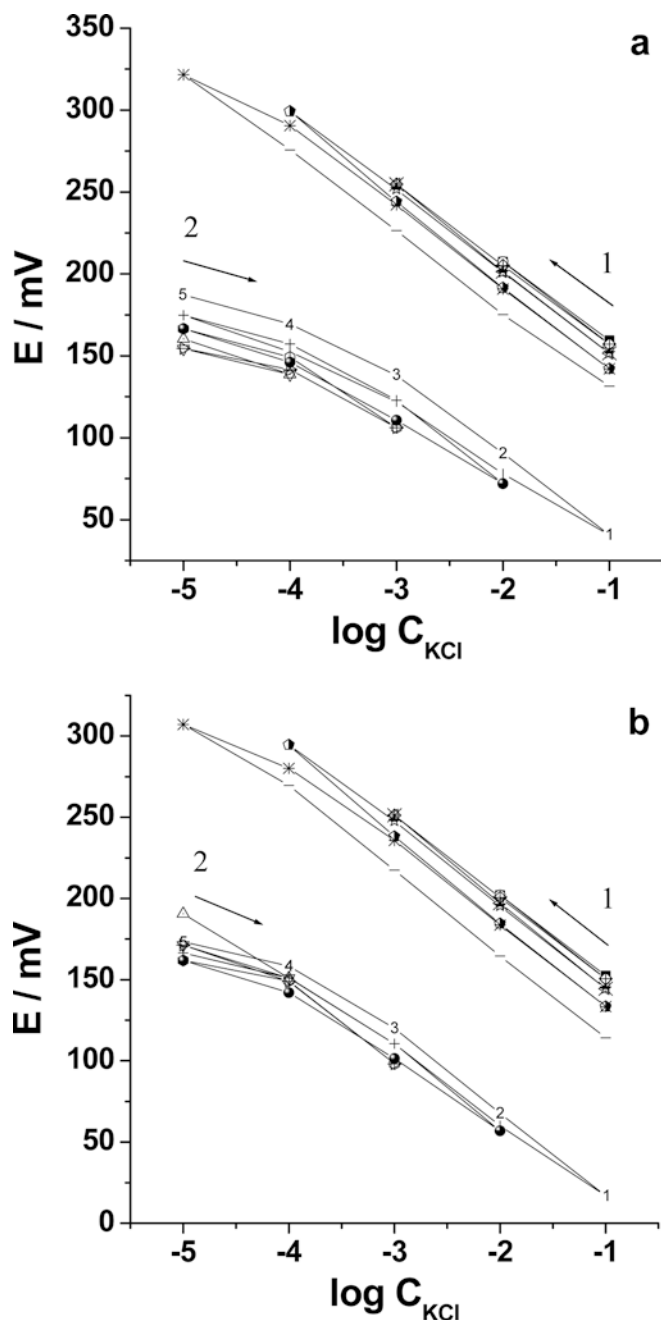
The potentiometric responses of the GC/PEDOT electrodes polymerized in solutions 1c and 2c were studied in KCl(aq), BM(aq) and BO(aq) solutions in the concentration range  $10^{-1}$ – $10^{-5}$  M. The electrodes were first conditioned in the calibration solution of the highest concentration ( $10^{-1}$  M) for 24 h. The calibration measurements were then started at the highest concentration ( $10^{-1}$  M) and the measurements were performed to successively lower concentrations, as follows:

$10^{-1} \rightarrow 10^{-2} \rightarrow 10^{-1} \rightarrow 10^{-2} \rightarrow 10^{-3} \rightarrow 10^{-2} \rightarrow 10^{-1} \rightarrow 10^{-2} \rightarrow 10^{-3} \rightarrow 10^{-4} \rightarrow 10^{-3} \rightarrow 10^{-2} \rightarrow 10^{-1} \rightarrow 10^{-2} \rightarrow 10^{-3} \rightarrow 10^{-4} \rightarrow 10^{-5} \rightarrow 10^{-4} \rightarrow 10^{-3} \rightarrow 10^{-2} \rightarrow 10^{-1}$  M.

Thereafter the electrodes were conditioned in the calibration solution of the lowest concentration ( $10^{-5}$  M) for 24 h and a new calibration measurement was made by starting at the lowest concentration, as follows:

$10^{-5} \rightarrow 10^{-4} \rightarrow 10^{-5} \rightarrow 10^{-4} \rightarrow 10^{-3} \rightarrow 10^{-4} \rightarrow 10^{-5} \rightarrow 10^{-4} \rightarrow 10^{-3} \rightarrow 10^{-2} \rightarrow 10^{-3} \rightarrow 10^{-4} \rightarrow 10^{-5} \rightarrow 10^{-4} \rightarrow 10^{-3} \rightarrow 10^{-2} \rightarrow 10^{-1} \rightarrow 10^{-2} \rightarrow 10^{-3} \rightarrow 10^{-4} \rightarrow 10^{-5}$  M.

A typical potentiometric response of the GC/PEDOT(BM) electrode in KCl(aq) solution is shown in Fig. 6a. The electrode shows an anionic response with a slope of about  $-50$  mV/decade. The anionic response indicates that the doping anions are mobile in the polymer and are able to be exchanged by the  $Cl^-$  ions at the polymer–solution interface. As can be seen in Fig. 6a, the standard potential continuously decreases during the measurement, so the potential difference between the first and last measurement point at  $10^{-1}$  M is about 30 mV. However, when the electrode is conditioned in a  $10^{-5}$  M KCl(aq) solution for 24 h and then successively immersed in higher concentrations, an anionic response with an increasing standard potential is observed. The slope in the potential range  $10^{-4}$ – $10^{-1}$  M is about  $-40$  mV/decade and the potential difference between the first and last measurement point is also here about 30 mV (Fig. 6a, calibration curve 2). Interestingly, the initial potential values in  $10^{-1}$  and  $10^{-5}$  M are about the same (about 0.2 V) after 24-h conditioning in each solution, despite the 4 orders of magnitude differ-



**Fig. 6** Potentiometric response of **a** GC/PEDOT(BM) and **b** GC/PEDOT(BO) in KCl(aq) solutions. Before measurement the electrode was conditioned for 24 h in  $10^{-1}$  M KCl (1) and  $10^{-5}$  M KCl (2)

ence in the concentrations ( $10^{-1}$  versus  $10^{-5}$  M). This indicates that the potential for the GC/PEDOT(BM) electrode gradually stabilizes at a certain potential (about 0.2 V) independent of the KCl concentration. This indicates that the potentiometric response to concentration/activity changes is only temporary. Similar results are obtained for the GC/PEDOT(BO) electrode, as shown in Fig. 6b. Comparative studies showed the same behavior also for PEDOT and polypyrrole doped with chloride (not shown). For polypyrrole doped with

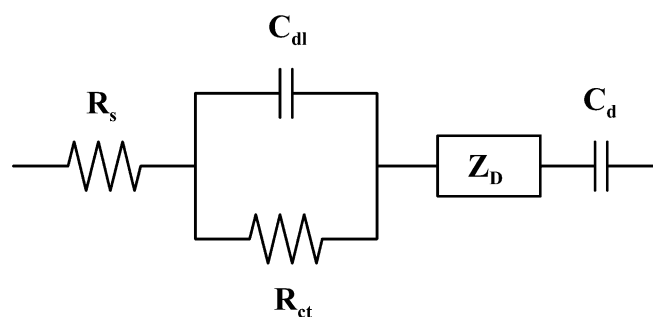
chloride the drift (towards about 0.2 V) is rapid than for PEDOT films prepared with the same polymerization charge (similar film thickness) [17]. The long-term potential drift may be ascribed to dissolved redox species, such as  $O_2/H_2O$ , gradually influencing the oxidation level and the standard potential of the polymer film electrode [13]. Such a mixed ionic–redox response is characteristic for conducting polymers, as described in detail earlier [13]. At low concentration of redox species in solution (and thick polymer films) the redox equilibrium is reached slowly compared with the ionic response and the redox interference may give rise to potential drift. However, the origin of the redox response was not studied in detail in this work. Traces of redox couples other than  $O_2/H_2O$  may also play a role.

The GC/PEDOT(BO) electrodes polymerized in BO/EDOT 1/1 (solution 2b) show an anionic response of about  $-52$  mV/decade in KCl(aq) solutions (concentration range  $10^{-1}$ – $10^{-4}$  M). The GC/PEDOT(BM) electrodes polymerized in BM/EDOT 1/1 (solution 1b) showed an anionic response of only about  $-35$  mV/decade in KCl(aq) solutions (concentration range  $10^{-1}$ – $10^{-4}$  M). Here, the small slope can be related to the very thin films of PEDOT(BM) [13].

The potentiometric response of the GC/PEDOT(BM) and GC/PEDOT(BO) electrodes in BM(aq) and BO(aq) solutions, respectively, reveal a sub-Nernstian anionic response in the concentration range  $10^{-2}$ – $10^{-5}$  M, with a slope of about  $-15$  to  $-40$  mV/decade. This indicates that it is a mixed anionic–cationic response. At the highest concentrations studied ( $10^{-2}$ – $10^{-1}$  M) the potential is almost constant, indicating an equal contribution from the cation ( $BMIM^+$ ) and anions ( $MDEGSO_4^-$  and  $OctSO_4^-$ ) to the electrode potential, or completely blocked ion exchange, as observed earlier also for polypyrrole doped with dodecyl sulfate [13].

#### Electrochemical impedance spectroscopy

EIS was performed at  $E_{dc} = 0.2$  V for GC/PEDOT(BM) and GC/PEDOT(BO) electrodes in different concentrations (0.05–2.0 M) of BM(aq) and BO(aq) solutions,



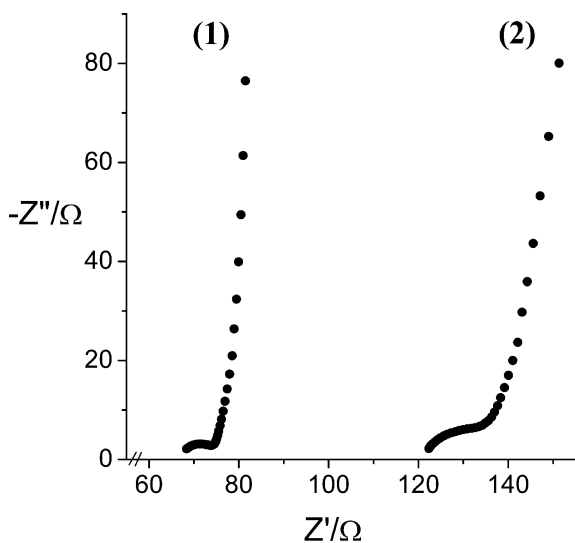
**Fig. 7** Equivalent electrical circuit for GC/PEDOT(BM) and GC/PEDOT(BO) electrodes. Solution resistance ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ), double-layer capacitance ( $C_{dl}$ ), finite-length Warburg diffusion impedance ( $Z_D$ ) and bulk redox capacitance ( $C_d$ )

respectively. The impedance spectra were fitted to the equivalent circuit shown in Fig. 7. As an estimation of the goodness of the fit, the  $\chi^2$  values were about 0.003–0.005. The circuit model is composed of the solution resistance ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ), double layer capacitance ( $C_{dl}$ ), bulk redox capacitance ( $C_d$ ) and the “classical” finite-length Warburg diffusion element ( $Z_D$ ).  $Z_D$  includes a diffusion capacitance ( $C_D$ ), a diffusional time constant ( $\tau_D$ ) and a diffusion resistance ( $R_D = \tau_D/C_D$ ) and can be described as follows [18]:

$$Z_D = \frac{(\tau_D/C_D) \coth(j\omega\tau_D)^{1/2}}{(j\omega\tau_D)^{1/2}}, \quad (2)$$

where  $\omega$  is the angular frequency ( $2\pi f$ ) and  $j = (-1)^{1/2}$ .

A similar circuit (without  $R_{ct}$  and  $C_{dl}$ ) was used earlier for PEDOT doped with chloride and poly(styrene sulfonate) in aqueous solutions [14]. Both the GC/PEDOT(BM) and GC/PEDOT(BO) electrodes in BM(aq) and BO(aq) solutions, respectively, show a high-frequency semicircle in the impedance spectra (Fig. 8), described by  $R_{ct}$  and  $C_{dl}$  in parallel. Such a semicircle was not seen for PEDOT doped with chloride or poly(styrene sulfonate) in aqueous solution [14]. The semicircle is observed for the GC/PEDOT(BM) and GC/PEDOT(BO) electrodes in all the aqueous solutions studied. The  $R_{ct}$  values for both GC/PEDOT(BM) and GC/PEDOT(BO) were found to decrease with increasing concentration of ionic liquid up to a certain limit where the values start to increase, as shown in Tables 2 and 3. Since  $R_{ct}$  depends on electrolyte concentration it can be related to ion transfer at the polymer–solution interface. Tables 2 and 3 also show that the  $R_{ct}$  values for GC/PEDOT(BO) are slightly higher than the values for GC/PEDOT(BM). The solution resistance  $R_s$  was



**Fig. 8** Complex plane impedance of GC/PEDOT(BM) in 1.5 M BM(aq) solution (1) and GC/PEDOT(BO) in 1.5 M BO(aq) solution (2). Frequency range 10 kHz–6.3 Hz.  $E_{dc} = 0.2$  V versus Ag

**Table 2** The resistance, capacitance and diffusional time constant values obtained by electrochemical impedance spectroscopy for GC/PEDOT(BM) in different concentrations of the ionic liquid BM(aq)

$C_{\text{ionic liquid}}/M$	$R_{ct}/\Omega$	$R_s/\Omega$	$R_D/\Omega$	$C_{\text{tot}}/\mu\text{F}$	$C_{CV}/\mu\text{F}$	$\tau_D/s$
0.05	31	357	219	298	342	0.9
0.1	6	230	129	314	361	0.5
0.5	5	78	38	317	398	0.1
1	5	63	38	345	414	0.1
1.5	4	80	54	325	430	0.2
2	12	92	113	345		0.4

found to follow the same concentration dependence as  $R_{ct}$  (Tables 2, 3).

The low-frequency part of the impedance spectrum (Fig. 8), described by  $Z_D$  and  $C_d$ , is related to ion diffusion in the polymer film and the bulk redox capacitance of the polymer [14]. The values of the diffusion resistance  $R_D$  for GC/PEDOT(BM) also show the same concentration dependence as  $R_{ct}$  and  $R_s$ , while the GC/PEDOT(BO) electrodes show the lowest  $R_D$  value at the highest concentration studied (2.0 M). The  $R_D$  values are higher for GC/PEDOT(BO) than for GC/PEDOT(BM) at a given concentration (Tables 2, 3).

The total polymer bulk redox capacitance ( $C_{\text{tot}}$ ) is given by two bulk capacitances ( $C_D$  and  $C_d$ ) connected in series as follows [14]:

$$C_{\text{tot}} = 1/(1/C_D + 1/C_d). \quad (3)$$

The total bulk capacitance of the polymer ( $C_{\text{tot}}$ ) increases slightly with increasing concentration of BM(aq) and BO(aq). The trend is clearer for the GC/PEDOT(BO) electrodes than for the GC/PEDOT(BM) electrodes (Tables 2, 3). The  $C_{\text{tot}}$  values for GC/PEDOT(BM) and GC/PEDOT(BO) are 298–345 and 370–480  $\mu\text{F}$ , respectively, in the concentration range (0.05–2.0 M) studied (Tables 2, 3).

The capacitance ( $C_{CV}$ ) values obtained by CV were calculated from the voltammograms as follows:

$$C_{CV} = I/v, \quad (4)$$

where  $I$  is the current and  $v$  is the potential scan rate. The current was obtained as the average values of the anodic and cathodic currents at  $E_{dc} = 0.2$  V. The  $C_{CV}$  values show a similar concentration dependence as the

**Table 3** The resistance, capacitance and diffusional time constant values for GC/PEDOT(BO) in different concentrations of the ionic liquid BO (aq)

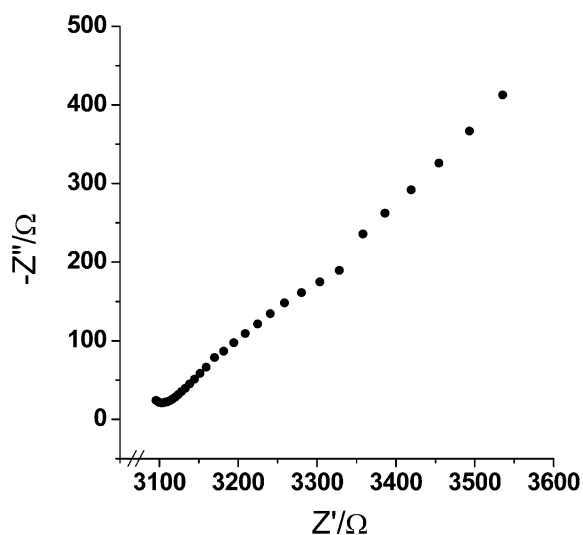
$C_{\text{ionic liquid}}/M$	$R_{ct}/\Omega$	$R_s/\Omega$	$R_D/\Omega$	$C_{\text{tot}}/\mu\text{F}$	$C_{CV}/\mu\text{F}$	$\tau_D/s$
0.05	36	702	653	370	442	1.3
0.1	22	506	429	374	438	1.0
0.5	14	176	321	379	459	1.0
1	7	122	300	395	482	1.8
1.5	9	124	270	405	505	1.8
2	18	155	204	418		0.7

$C_{\text{tot}}$  values from EIS (Tables 2, 3); however, the absolute values of  $C_{\text{CV}}$  are higher than those of  $C_{\text{tot}}$ , as observed earlier also for PEDOT doped with chloride and poly(styrene sulfonate) [14]. Such a discrepancy is commonly observed for conducting polymers and one possible explanation is the intrinsic hysteresis of the doping/undoping process resulting in a smaller amount of charge being transferred in EIS owing to the small amplitude of the excitation signal, i.e., a very narrow potential window (10–20 mV) in comparison with that employed in CV (1,000 mV) [19, 20].

The diffusional time constant ( $\tau_{\text{D}}$ ) values for the GC/PEDOT(BM) and the GC/PEDOT(BO) electrodes are about 0.1–0.9 and 0.7–1.8 s, respectively (Tables 2, 3).

Altogether, these EIS results indicate slightly faster ion transport in BM(aq) than in BO(aq) at a given concentration (0.05–2 M). The slightly higher bulk redox capacitance for GC/PEDOT(BO), compared with that for GC/PEDOT(BM), can therefore be related to a higher yield of electroactive material when using BO as an electrolyte during electropolymerization.

The impedance spectrum of the GC/PEDOT(BM) electrode in pure BM (about 3.8 M) is dominated by an about 45° diffusion line (Fig. 9), indicating diffusion control of the doping/undoping process in BM. Also the solution resistance  $R_s$  was found to be very high (about 3.1 k $\Omega$ ) in pure BM. This indicates slow ion transport in the pure ionic liquid (BM) as well as in the polymer film contacted with pure ionic liquid (BM).  $R_s$  decreases by more than 1 order of magnitude when BM is diluted with water to a concentration of 2 M (Tables 2, 3). These results show that water increases the ion mobility both in the ionic liquid and in the conducting polymer film.



**Fig. 9** Complex plane impedance of GC/PEDOT(BM) in pure BM. Frequency range 10 kHz–6.3 Hz.  $E_{\text{dc}} = 0.2$  V versus Ag

## Conclusions

In this work, two different ionic liquids, BM and BO, and their aqueous solutions were used as electrolytes in electropolymerization of EDOT. BM is in liquid form and BO is in solid form at room temperature. The only successful polymerization in a water-free ionic liquid solution occurred in a BO/EDOT 1/1 solution. The electropolymerization in a BM/EDOT 1/1 solution resulted in a very thin polymer film and no polymer was formed on the electrode during electropolymerization in pure BM containing 0.1 M EDOT. However the electropolymerizations were successful in 1.5 M aqueous solutions of the ionic liquids containing 0.1 M EDOT. The polymerization potential was significantly lower in BO than in BM solutions, which can be related to the amphiphilic (surfactant) properties of  $\text{OctSO}_4^-$ .

Both GC/PEDOT(MDEGSO<sub>4</sub>) and GC/PEDOT(OctSO<sub>4</sub>) show an anionic potentiometric response in KCl(aq) solution, indicating that the doping anions (MDEGSO<sub>4</sub><sup>-</sup> and OctSO<sub>4</sub><sup>-</sup>) are mobile inside the polymer and are able to be exchanged by the Cl<sup>-</sup> ions at the polymer–solution interface. However, in BM(aq) and BO(aq) solutions the contribution from the BMIM<sup>+</sup> cation suppresses the anionic response at higher concentrations of the ionic liquids in water (10<sup>-2</sup>–10<sup>-1</sup> M).

The impedance measurements show that the solution resistance in pure BM is high (about 3.1 k $\Omega$ ). Dilution of BM with water leads to a dramatic decrease in the solution resistance and also increases the rate of ion diffusion in the polymer film. EIS results indicate slightly faster ion transport in BM(aq) than in BO(aq) at the same concentration (0.05–2 M). The slightly higher bulk redox capacitance for GC/PEDOT(BO), compared with that for GC/PEDOT(BM), can be related to a higher yield of electroactive material when using BO as an electrolyte during electropolymerization.

**Acknowledgements** Financial support from the Academy of Finland is gratefully acknowledged. This work is part of the activities at the Abo Akademi Process Chemistry Group within the Finnish Centre of Excellence Programme (2000–2005) by the Academy of Finland.

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