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# Electrochemical studies of heterogeneous reduction of tetracyanoquinodimethane in poly(ethylene oxide) electrolytes using ac impedance and cyclic voltammetry at an ultramicroelectrode

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Received 26th May 2000, Accepted 4th October 2000 First published as an Advance Article on the web 9th November 2000

Electrochemical studies of the TCNQ<sup>0</sup>/TCNQ<sup>-</sup> couple have been carried out using ac impedance spectroscopy and cyclic voltammetry at platinum ultramicroelectrodes (UME). Liquid poly(ethylene oxide) (PEO) CH<sub>3</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>4</sub>-CH<sub>3</sub> has been used as the solvent with different concentrations of the TCNQ<sup>0</sup>/TCNQ<sup>-</sup> couple and LiClO<sub>4</sub> as the supporting electrolyte. On the basis of the ac impedance results at the UME it has been found that the double layer capacitance and standard heterogeneous rate constant are independent of the presence of electroactive species and supporting electrolyte concentrations, indicating that adsorption of electroactive species onto the electrode is not significant. The standard heterogeneous rate constant  $k_s$  was found to be  $0.109 \pm 0.005$  cm s<sup>-1</sup>. A similar value of  $k_s = 0.094$  cm s<sup>-1</sup> was obtained for the second reduction step TCNQ<sup>-</sup>/TCNQ<sup>2-</sup>. Diffusion coefficients of both TCNQ and TCNQ<sup>-</sup> are equal,  $D = 1.0 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> for a 0.5 M LiClO<sub>4</sub> solution. Higher diffusion coefficients are obtained in less concentrated supporting electrolyte. Comparison is made between these results and those reported previously for PEO-400 HO-(CH<sub>3</sub>CH<sub>2</sub>O)<sub>8</sub>-OH.<sup>1</sup> The different end groups significantly influence the viscosity and hence  $k_s$ .

# Introduction

Interest in polymer electrolytes is growing rapidly because of their potential applications in batteries, fuel cells, sensors, *etc.* As a result, understanding their fundamental electrochemistry is becoming of considerable importance.<sup>1–13</sup> Central to this is a better understanding of the nature of redox reactions in these solid solvents.

Polymer electrolytes may be prepared with the same chemical composition but very different molar mass, ranging from low molecular weight liquids through to solids with molar masses of several million. The dynamics of the solvent varies significantly with molar mass and as a result polymer electrolytes offer an unprecedented medium for the study of the influence of solvent dynamics on the kinetics of electron transfer. This is a problem of wide scientific importance—such processes lie at the core of many chemical, physical and biological phenomena. Due to the importance of the influence of solvent molar mass on the standard rate constant, such studies have been also reported previously.<sup>1–6,8–13</sup> The understanding, however, of this phenomena is far from complete.

Poly(ethylene oxide) (PEO)– $(CH_2-CH_2-O)_n$  has proved to be a particularly effective solvent for polymer electrolytes. Dissolution of salts in this solvent is driven by the coordination of the cations by the ether oxygens. As a result solubility is high for salts based on monoatomic cations but lower for polyatomic cations. A suitable redox system to study electron transfer should be the anionic couple TCNQ<sup>0</sup>/TCNQ<sup>-</sup> in which both oxidised and reduced forms are soluble in PEO. Usage of this couple avoids the complications of metal ions and solubility in testing electron transfer models in such a viscous solvent as PEO. It should be noted that this couple was used in the past to investigate the influence of solvent relaxation dynamics on the homogeneous charge transfer process in a non-aqueous solvent.<sup>14-18</sup>

The purpose of the present paper is to report on the basic electrochemistry of the TCNQ<sup>0</sup>/TCNQ<sup>-</sup> couple in the low molecular weight PEO CH<sub>3</sub>O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>4</sub>-CH<sub>3</sub> (tetramer). We expect that a credible redox system for the study of the electron transfer in viscous solvents can be established as a result of our study. PEO is normally terminated by OH groups. In the case of a low molecular weight liquid this becomes a significant proportion of the solvent and can greatly affect the solvent dynamics, coordination of the salt and other properties. CH<sub>3</sub>-termination ensures that the low molecular weight ethers are chemically similar to high molecular weight PEO. A previous study of TCNQ in low molecular weight PEO has employed an OH terminated solvent.<sup>1</sup> Murray and co-workers have studied the kinetics of electronic self-exchange (homogeneous e<sup>-</sup> transfer) between TCNQ<sup>0</sup> and TCNQ<sup>-</sup>.<sup>12,13</sup>

In the present paper we have carried out investigations of heterogeneous charge transfer process at solid Pt ultramicroelectrodes (UME) in tetramer as a function of the TCNQ<sup>0</sup>/ TCNQ<sup>-</sup> and supporting electrolyte concentrations. Steady-state voltammetry and ac impedance methods have been applied. Ac impedance measurements at the UME proved to be a very effective method for studying the mechanism and kinetics of electrochemical processes in aqueous, non-aqueous and polymer electrolytes.<sup>4,19–21</sup> It should be stressed that the results presented in this work were obtained using an argon filled Mbraun glove box and distilled PEO. These procedures have been employed to minimise the influence of the impurities on the charge transfer kinetics studies. It is well known (and unfortunately not sufficiently appreciated) that the presence of impurities such as water and oxygen can significantly influence the kinetic results of solid electrodes in non-aqueous solvents.

# Experimental

## Chemicals

Tetraethyleneglycol dimethyl ether  $[CH_3-O-(CH_2-CH_2-O)_4-CH_3]$ , abbreviated here to tetramer (Aldrich 99%), was purified by vacuum distillation at  $10^{-3}$  mbar and 147 °C using a Fischer HMS 500C distillation apparatus with 90 theoretical plates. 7,7,8,8-Tetracyanoquinodimethane (TCNQ, Aldrich 98%) was purified by sublimation under vacuum at 258 °C.

Lithium tetracyanoquinodimethane (LiTCNQ) was prepared by the reaction of purified TCNQ and lithium iodide in high purity acetonitrile. The purple crystals obtained were filtered off and washed with acetonitrile until they became bright green in colour. The solid was then washed with a large volume of ether.

Lithium perchlorate (LiClO<sub>4</sub>, Aldrich 99 + %) was dried by heating the salt at  $160 \degree$ C for 48 h under vacuum.

All samples were transferred to an argon filled Mbraun glove box for storage. Typically the water and oxygen levels inside the box were less than 0.05 ppm.

#### **Electrodes and cells**

Electrochemical measurements were performed using a standard two-electrode cell. The working electrode was a platinum microdisc with a diameter of either 10 or 20  $\mu$ m (Rudawski Ventures, Poland). Before each measurement the working electrode was polished using 0.05  $\mu$ m alumina powder and rinsed using tetramer. The counter/reference electrode consisted of a coiled platinum wire immersed in an equimolar tetramer solution of 5 mmol dm<sup>-3</sup> of both LiTCNQ and TCNQ with 0.5 M LiClO<sub>4</sub>. The body of this electrode consisted of a glass tube closed at one end by a Vicor glass frit attached with heat shrinking Teflon. The electrochemical cell was placed inside a Faraday cage, which in turn was situated inside the glove box.

#### Apparatus and procedures

Experiments were carried out on equimolar solutions of TCNQ and LiTCNQ in the concentration range  $0.1-10 \times 10^{-3}$  mol dm<sup>-3</sup>, with the concentration of the supporting electrolyte (LiClO<sub>4</sub>) being either 0.1 or 0.5 mol dm<sup>-3</sup>.

Linear sweep voltammetry, in the range +0.3 V to -0.3 V, was carried out using an Autolab PGSTAT-10 (Eco Chemie) with a low current (ECD) module.

For ac impedance spectroscopy measurements the working electrode was connected to the input of a EG&G PAR preamplifier 181, the output of which was connected directly to the input of a Solatron 1255 Frequency Response Analyser. The generator output of the 1255 was connected to both the voltage input and the counter electrode. Coaxial cables were used to connect the EG&G preamplifier to the 1255 and to the cell, the sheaths of the coaxial cables were grounded. Measurements were under the control of an IBM PC. An ac signal of between 5 and 10 mV rms was employed and data was collected in the frequency range 0.01 Hz to 250 kHz.

#### Analysis of ac impedance results

The theoretical analysis of the diffusion process to a microdisc has been given by Fleischmann and Pons<sup>22</sup> who proposed an equivalent circuit, which can be used to analyse the experi-

mental results. We have shown,<sup>4,19-21</sup> that this equivalent circuit does represent the experimental data, but the analysis of such data may be greatly facilitated by using an equivalent circuit which is appropriate to a hemispherical electrode (Fig. 1). In this case the diffusional impedance of the microdisc is represented by a parallel combination of a Warburg impedance,  $Z_w$ , and resistance,  $R_{nl}$ , which is related to non-linear (hemispherical) diffusion. The appropriate equations describing both the  $Z_w$  and the  $R_{nl}$  can be found in the literature.4,19-22 At high frequencies the ac impedance response of the microdisc is dominated by the charge transfer resistance,  $R_{\rm ct}$ , and double layer capacitance,  $C_{\rm dl}$ , and, as a consequence, a semicircle may be observed in the complex plane. At these frequencies, the diffusion is generally linear and semi-infinite, corresponding to a Warburg response,  $Z_w$ . At low frequencies, and in contrast to the situation with electrodes of normal dimensions, the diffusion becomes spherical (non-linear). Of course the relative values of the electrochemical parameters influence the overall shape of the impedance. When  $R_{\rm ct}$  is large, the high frequency semicircle dominates since the charge transfer kinetics largely control the electrochemical response. On the other hand, when  $R_{ct}$  is small, the diffusional impedance dominates and the low frequency diffusional quartercircle becomes prominent. However, even in this case, the electrochemical parameter  $k_s$  (standard heterogeneous charge transfer constant) makes a significant contribution to the value of the impedance in at least part of the frequency range. The shape of the diffusional part of the Nyquist graph depends on the non-dimensional frequency:  $a^2\omega/D$ , where a is the ultramicroelectrode radius,  $\omega$  angular frequency and D is the diffusion coefficient of the electroactive species. It can be shown that for high values of UME radius and low values of the diffusion coefficient the influence of non-linear diffusion is not dominant and the steady-state impedance cannot be achieved for frequencies as low as several mHz.

The experimentally recorded impedance spectra are always influenced by unwanted elements such as outer inductance (which is negligible) and electrolyte resistance. Their values were removed prior to the evaluation of the charge transfer resistance and diffusion impedance. As seen in Fig. 2, where an example of a fit obtained using Boukamp's<sup>23</sup> program is presented as a Bode plot, the fit is excellent in the whole frequency range from 1 Hz to 100 kHz. It should be added that in the present work the influence of the outer inductance can be neglected and consequently it is not presented in Fig. 1.

After removal from the recorded impedance spectra of the contribution of the unwanted outer elements their remaining part was worked out in terms of a simple model consisting of a single charge transfer step with diffusion described by equations derived for the hemispherical approximation of the UME by Los and Bruce<sup>19–21</sup> who showed that the approximation is valid over the whole frequency range used in this



**Fig. 1** Equivalent circuit used for analysis of the experimental ac impedance results:  $R_{\rm s}$ —the electrolyte resistance,  $R_{\rm ct}$ —the charge transfer resistance,  $C_{\rm dl}$ —the double layer capacitance,  $Z_{\rm w}$ —Warburg impedance,  $R_{\rm nl}$ —the resistance due to the non-linear diffusion.



Fig. 2 The ac impedance data obtained in 10 mM TCNQ/LiTCNQ in tetramer solution with 0.5 M LiClO<sub>4</sub> at a platinum UME of 20  $\mu$ m radius using Boukamp's program.<sup>23</sup> (O) experimental results, (+) NLLSFit.

work. An example of such a NLLSFit obtained by a special FORTRAN program<sup>24</sup> is presented in Fig. 3.

## **Results and discussion**

Fig. 4 presents voltammetry curves obtained at a sweep rate of 50 mV s  $^{-1}$  using 10 and 20  $\mu m$  Pt UMEs and 5 mM TCNQ/ TCNQ  $^-.$ 

Two reduction waves are observed with approximately the same heights for both electrodes. They are associated with the following two one-electron reduction steps:<sup>12,13</sup>

$$TCNQ^{0} + 1e^{-} = TCNQ^{-}, \quad E^{\circ\prime}(1) = 0 V$$
 (1)

$$TCNQ^{-} + 1e^{-} = TCNQ^{2-}, \quad E^{\circ\prime}(2) = -0.55 \text{ V}$$
 (2)

The separation of the potentials for the two reduction steps,  $E^{\circ\prime}(1) - E^{\circ\prime}(2) = 0.55$  V, is the same as that reported previously for TCNQ in non-aqueous and solid polymer electrolytes. A steady-state response is obtained at the 10 µm electrode whereas planar diffusion contributes to the response observed at the 20 µm UME. An almost ideal steady-state response is observed for the TCNQ<sup>0</sup>/TCNQ<sup>-</sup> couple within the range 0.1–10 mM. The steady-state current is proportional to the TCNQ<sup>0</sup>/TCNQ<sup>-</sup> concentration and the approximately equal magnitudes of the two waves indicate that the diffusion



Fig. 3 The ac impedance data obtained in 10 mM TCNQ/LiTCNQ in tetramer with 0.5 M LiClO<sub>4</sub> solution at a platinum UME of 20  $\mu$ m radius. McDonald's CNLS procedure<sup>24</sup> was used: (O) experimental results, (+) NLLSFit.



Fig. 4 Experimental CV curves obtained in 5 mM TCNQ/LiTCNQ in tetramer with 0.5 M LiClO<sub>4</sub> solution at platinum UMEs of 20 and 10  $\mu$ m radius; sweep rate 0.05 V s<sup>-1</sup>.

coefficients of the oxidised and reduced forms are approximately equal.

A value of  $1.08 \pm 0.02 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> (the average of 12 cyclic voltammetry measurements) was calculated for the TCNQ<sup>0</sup>/TCNQ<sup>-</sup> diffusion coefficients in 0.5 M LiClO<sub>4</sub>, based on the equation for steady-state current ( $I_{s-s}$ ) at an ultramicrodisc electrode,  $I_{s-s} = 4nFDCa$ , where *a* is the radius of the UME, *C* the concentration of TCNQ<sup>0</sup> and TCNQ<sup>-</sup> and *D* the diffusion coefficient. The geometric radius of the electrode was used to calculate the diffusion coefficients. As might be expected, the steady-state current is proportional to the radius of UME. The diffusion coefficient is around 30% higher in 0.1 M LiClO<sub>4</sub> electrolyte (Fig. 5), which may be explained by the lower viscosity of the more dilute electrolytes.

The kinetics of the first reduction step has been studied by ac impedance measurements. Fig. 6 presents ac impedance responses with and without electroactive species.

With only supporting electrolyte present in the solution a straight, almost vertical line is observed which can be described by an equivalent circuit consisting of the solution resistance  $R_s$  in series with the double layer capacitance  $C_{dl}$ . This description can be improved by replacing  $C_{dl}$  with a constant phase element (CPE).<sup>25</sup> The impedance of CPE is equal to  $1/[A(j\omega)^{\phi}]$  where  $j = \sqrt{-1}$ , A is a constant,  $\phi$  an exponent <1 and  $\omega$  is the angular frequency of the ac signal. The deviation from an ideal capacitor arises from the roughness of the



Fig. 5 Experimental CV curves obtained in 5 mM TCNQ/LiTCNQ in tetramer with 0.1 and 0.5 M LiClO<sub>4</sub> solutions at a platinum UME of 10  $\mu$ m radius, sweep rate 0.01 V s<sup>-1</sup>.



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10 µm radius; (b) Pt UME of 20 µm radius; in tetramer with 1 mM TCNQ/LiTCNQ with 0.5 M LiClO<sub>4</sub> and in tetramer with 0.5 M LiClO<sub>4</sub>.

electrode surface. The expression for the CPE can be related to the fractal dimension of the surface.<sup>25</sup> In the system studied here, the near vertical nature of the line, corresponding to an exponent of 0.97, implies a relatively smooth surface. Because of this we shall treat the interface as a capacitor, the value of which varies from 15 to 40  $\mu$ F cm<sup>-2</sup>. With the electroactive couple present in the solution the ac impedance response is typical for the ultramicrodisc, as seen in Fig. 6. The diffusional impedance, which consists of parallel combination of  $Z_w$  and  $R_{\rm nl}$ , is represented by a quarter-circle on the complex plane. Fig. 6 shows that the uncompensated solution resistance  $R_s$  is small in comparison to the faradaic impedance. Additionally, in all cases  $R_{\rm s}$  and  $R_{\rm ct}$  are in the same range (~0.1–1.0  $\Omega$  cm<sup>2</sup>), showing high accuracy in the ac impedance evaluation of the standard heterogeneous charge transfer constant,  $k_s$ .

According to the theory of ac impedance a minimum value of the charge transfer resistance and diffusional impedance should be obtained at the half-wave potential  $(E^{\circ\prime}(1) = 0.00)$ V), assuming a simple charge transfer mechanism. Fig. 7 shows the dc potential dependence of the ac impedance response.

A minimum impedance is obtained at dc potentials approaching 0.00 V. The experimental curves have been analysed according to a simple mechanism consisting of a single charge transfer step with diffusion. Fig. 8 shows that the model described by equations derived by Los and Bruce<sup>19</sup> provides a good fit to the data.

The fit has been carried out using four adjustable parameters: double layer capacitance  $C_{dl}$ , heterogeneous charge transfer constant  $k_s$ , diffusion coefficient D and radius a of the UME. Very similar numeric results for the fit can be obtained when using the voltammetric diffusion coefficients and geometric radius of the electrodes as fixed parameters. In this case



Fig. 7 The dc potential dependence of the ac impedance results obtained in 10 mM TCNQ/LiTCNQ solution in tetramer with 0.5 M LiClO<sub>4</sub> at a platinum UME of 10  $\mu$ m radius.

only two adjustable parameters are used:  $C_{dl}$  and  $k_s$ . However, it is recommended to verify ac impedance measurements using adjustable parameters (in this case D and a) which can be determined by other methods. Table 1 presents the actual exemplary values of these parameters obtained by the fit procedures. It should be noticed that relatively low values (lower than 5%) of the standard deviations of the parameters were obtained. This proves the very good quality of the fit and directly confirms the appropriate choice of the equivalent circuit.

Double layer capacitance values ranging from 20 to 40 µF  $cm^{-2}$  have been obtained. Given that the measurements in the absence of the redox couple showed that the surface is not perfectly smooth, some variations in  $C_{\rm dl}$  extracted from the ac data obtained in the presence of the redox couple is to be expected. The error reflects different  $C_{d1}$  values (different roughnesses) for different electrodes, but the error on any one electrode is much smaller. It is clear from examination of the values given in Table 2 that diffusion coefficients for the electroactive species in 0.1 M LiClO<sub>4</sub> solutions are higher than in 0.5 M LiClO<sub>4</sub> electrolytes. This is consistent with the results described above for the steady-state measurements.

It should be noted that the values for D were obtained, in the case of the ac data, using the fitted area of the electrode whereas the geometrical area was used in the analysis of the CV data. This may account for the small discrepancy in the absolute values of D measured by the two methods.



Fig. 8 The ac impedance data obtained in 10 mM TCNQ/LiTCNQ solution in tetramer with 0.5 M LiClO<sub>4</sub> at a platinum UME of 20  $\mu$ m radius. The equivalent circuit derived by Los and Bruce<sup>19</sup> was used (explanation in text): (O) experimental results, (+) NLLSFit.

 Table 1
 Parameters obtained by the fit procedure<sup>a</sup>

LiClO <sub>4</sub> /M	TCNQ <sup>0</sup> /TCNQ <sup>-</sup> /mM	Dc pot./mV	$C_{\rm dl}/\mu{\rm F~cm^{-2}}$	$D/1.0 \times 10^{6} \text{ cm}^{2} \text{ s}^{-1}$	r/µm	$k_{\rm s}/{\rm cm~s^{-1}}$
0.1	5	0	32.6	1.07	11.6	0.103
0.5	5	0	27.6	0.66	11.5	0.138
0.5	10	0	42.1	0.57	12.2	0.122
0.5	10	-20	35.0	0.50	12.4	0.139
0.5	10	+20	24.8	0.52	11.5	0.102

<sup>*a*</sup> All values presented are actual exemplary results of the fit to the experimental ac impedance results. The quality of the fit is described by the standard deviations of these parameters, which do not exceed 5%.

Table 2 Average values and the averages' standard deviations of the parameters determined by the fit to the experimental results

Conc. of LiClO <sub>4</sub> /M	$k_{\rm s}/{\rm cm~s^{-1}}$	$C_{\rm dl}/\mu{\rm F~cm^{-2}}$	$D/1.0 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$			
0.1	$0.098 \pm 0.022$	$29.6 \pm 8.6$	$0.98\pm0.08^a$			
0.5	$0.112 \pm 0.027$	$20.9 \pm 10.8$	$0.75 \pm 0.05^b$			
<sup>3</sup> Seven measurements at dc potentials ranging from $-10$ to $+10$ mV <sup>b</sup> Nineteen measurements at dc potentials ranging from $-40$ to $+40$ mV						

Table 2 shows that double-layer capacitance and standard heterogeneous rate constant are independent of the supporting electrolyte concentration within experimental error.

The electrochemical reduction of TCNQ is a relatively fast reaction, consistent with observations of the homogeneous self-exchange rate constants for that couple (around  $1.0 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> in a non-aqueous solvent of low viscosity such as acetonitrile<sup>12,13</sup>). The values of the double-layer capacitance are slightly higher than for pure supporting electrolyte but they show no evidence of adsorption of the reactants.

Using the same analysis the following kinetic parameters have been obtained in 0.5 M LiClO<sub>4</sub> for the second reduction step described by reaction (2):  $k_s = 0.094$  cm s<sup>-1</sup>,  $D = 1.30 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> and  $C_{dl} = 10$  µF cm<sup>-2</sup>. An advantage of using ac impedance measurements is that the faradaic and non-faradaic parameters may be obtained within the same experiment. The importance of fitting both faradaic and non-faradaic and finding that  $C_{d1}$  is the same in the presence and absence of reactant is to gain confidence that the fitting procedure produces reliable results. The invariance of the double-layer capacitance and the standard rate constant with concentration demonstrate that there appears to be no complications in the interpretation of the redox reaction (such as ion pairing). This was especially important in our studies since a double-layer effect has been suggested by Zhou et al.<sup>1</sup> These results are in a good agreement with the findings of the Pyati and Murray<sup>6</sup> concerning cobalt tris(bipyridine) oxidation in liquid polymer electrolytes of different molecular weight.

Although the ac impedance data have been analysed successfully in terms of a simple electrode reaction, we cannot rule out the possibility that the redox active species may not be TCNQ or TCNQ<sup>-</sup> (as it is written in reactions (1) and (2)). In particular ion pairing between TCNQ<sup>-</sup> and Li<sup>+</sup> is possible in such a low dielectric constant solvent ( $\varepsilon = 9$ ). Fast sweep cyclic voltammetry is currently being employed to investigate further the possibility of ion pairing.

It is interesting to compare our results with those of Zhou et al.<sup>1</sup> who used OH terminated PEO of molecular weight 400 which, like tetramer, is a liquid at room temperature. They obtained the following kinetic data for the TCNQ/TCNQ-couple in 0.1 LIClO<sub>4</sub>:  $k_s = 0.00037$  cm s<sup>-1</sup> and  $D = 2.5 \times 10^{-8}$  cm s<sup>-1</sup>. Their standard rate constant is some 300-fold and the diffusion coefficient 40-fold lower than in tetramer. The electron transfer rate is dependent on the longitudinal relaxation time of the solvent,  $\tau_L$ , which is in turn related to the solvent viscosity.<sup>6,26–29</sup> The differences in the kinetic parameters between the two solvents are consistent with the observation that the solvent viscosity of PEO-400 is

some 20-fold higher (0.889 P) than that of tetramer. The influence of  $\tau_{\rm L}$  is particularly strong when comparing these two solvents because of the similarity of the dielectric constant and hence the Pekar factors. These correlations ignore the specific chemical differences between the chain ends in the two solvents. The OH groups are likely to bind preferentially to the Li<sup>+</sup> ions and it is known that electron transfer rates can be different in solvents containing OH groups compared with those that do not.<sup>6,8,12</sup>

### Conclusions

TCNQ<sup>0</sup>/TCNQ<sup>-</sup> appears to be a suitable couple for probing solvent relaxation in PEO, as it appears to show no complications due to complexation or adsorption at the electrode in 0.1 to 0.5 M LiClO<sub>4</sub> in a PEO electrolyte system. This allows the influence of solvent dynamics on the heterogeneous charge transfer process to be probed. We have used ac impedance at an UME to determine  $k_s$  and D for the redox couple in the tetramer. Values for these parameters in 0.5 M LiClO<sub>4</sub> in PEO are  $k_s = 0.11 \pm 0.05$  cm s<sup>-1</sup> and  $D = 0.75 \times 10^{-6}$  cm s<sup>-1</sup>. They are significantly higher than found previously for PEG-400 where  $k_s = 0.00037$  cm s<sup>-1</sup> and  $D = 2.5 \times 10^{-8}$  cm  $s^{-1}$ .<sup>1</sup> These differences can be explained in terms of the different end groups (OH in the case of PEG-400) and by the great differences in viscosities of the solvents used (tetramer: 0.0339 P and PEG-400: 0.889 P). Contrary to the PEG-400 study<sup>1</sup> we find no dependence of  $k_s$  on the supporting electrolyte concentration. The kinetics of the second reduction step TCNQ<sup>-</sup>/ TCNQ<sup>2-</sup> have also been studied using ac impedance at an UME and the following values of the kinetic parameters obtained:  $k_s = 0.098 \text{ cm s}^{-1}$  and  $D = 1.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

# Acknowledgements

This work has been supported by the Polish Scientific Committee (KBN), grant No. 0344/T09/98/15.

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