NMR measurements of self diffusion in polymer gel electrolytes

M.J. Williamson, H.V.St.A. Hubbard, I.M. Ward[*]

IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK

Abstract

The pulsed field gradient NMR spin-echo technique has been used to measure the self diffusion coefficients of solvent molecules, Li^+ cations and $CF_3SO_3^{-1}$ anions in polyvinylidene fluoride (PVDF) gel electrolytes incorporating liquid electrolytes based on either *N,N*-dimethylformamide (DMF) or tetraglyme (TG) and lithium triflate (LiT). Using the Nernst–Einstein equation with the NMR diffusivities, calculated values for the ionic conductivity were obtained and compared with those determined by ac conductivity measurements to provide estimates of ionic association. These results for the gel electrolytes are compared with those for the corresponding liquid electrolytes, over a range of salt concentrations and temperatures. In general terms, the comparisons support the simple conclusion that regions of liquid electrolyte exist within the gel electrolytes, consistent with limited measurements of the transverse relaxation time T_2 on these systems, which are also reported. There are, however, some small but significant differences between the behaviours of the gel electrolytes and the liquid electrolytes and these are discussed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Pulsed field gradient NMR measurements; Polymer gel electrolyte; Self diffusion

1. Introduction

In previous articles pulsed field gradient (PFG) spin-echo NMR measurements of the self diffusion coefficients of solvent molecules (^{1}H measurements), Li^+ cations ([7]Li measurements) and $CF_3SO_3^-$ anions (^{19}F measurements) have been reported for liquid electrolytes based on lithium trifluoromethanesulphonate (lithium 'triflate', LiT) and either *N,N*-dimethylformamide (DMF) or tetra(ethylene glycol) dimethyl ether ('tetraglyme', TG) [1,2]. In addition, measurements of the NMR longitudinal relaxation time T_1 have been reported for these systems [3]. In combination with measurements of ionic conductivity and viscosity, the NMR measurements have been shown to be extremely valuable in providing quantitative information on issues such as the degree of ionic association and the mechanisms of ionic mobility. Similar NMR studies have been reported by other groups [4,5].

Recent research at Leeds University has focused on the behaviour of gel electrolytes [6,7], where a polymer is dissolved in the liquid electrolyte at high temperatures. On cooling, a thermoreversible gel is produced where the liquid electrolyte is now contained in a polymeric matrix. Such systems can show high levels of ionic conductivity and excellent mechanical properties. In the case of gel electrolytes based on PVDF, tough transparent materials are produced with room temperature conductivities in the range of 10^{-3} S cm^{-1} (DMF) to 10^{-4} S cm^{-1} (TG).

The present article describes PFG spin-echo NMR measurements on PVDF gel electrolytes incorporating either DMF/LiT or TG/LiT liquid electrolytes. As expected, there are many similarities between the behaviour of the gel electrolyte and the corresponding liquid electrolytes, but some minor differences also exist, which are interesting to discuss.

2. Experimental

2.1. Preparation of gel electrolytes

The materials required for the preparation of PVDF gel electrolytes were obtained from Aldrich and dried prior to use. For the solvents, DMF and tetraglyme, the drying was achieved by storage over a 3 Å molecular sieve, while PVDF (in powder form, molecular weight = 534 000) and lithium triflate were dried in a vacuum oven for at least 48 h prior to use at 100 and 130°C, respectively.

Initially, liquid electrolytes were prepared in an oxygen-free nitrogen atmosphere by dissolving the appropriate amount of lithium triflate in either DMF or tetraglyme. Weighed amounts of PVDF were then added to each liquid

* Corresponding author. Tel: + 44-0113-2333808; fax: + 44-0113-2333846.

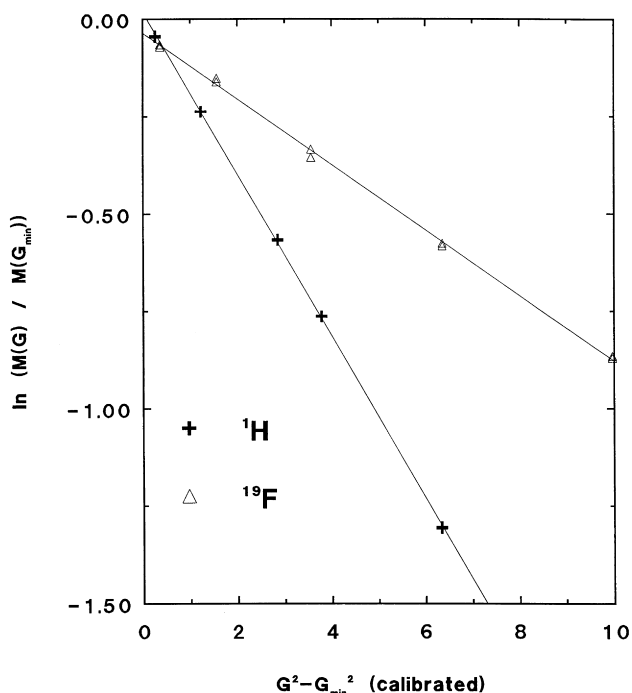*E-mail address:* i.m.ward@leeds.ac.uk (I.M. Ward)

Fig. 1. Representative plots of $\ln\{M(G)/M(G_{\min})\}$ against $(G^2 - G_{\min}^2)$ for a PVDF/DMF/LiT gel (see text for details of salt concentration and temperature).

electrolyte, which were heated and stirred intermittently until homogeneous mixtures were observed. Upon cooling, thermoreversible polymer gel electrolytes were formed.

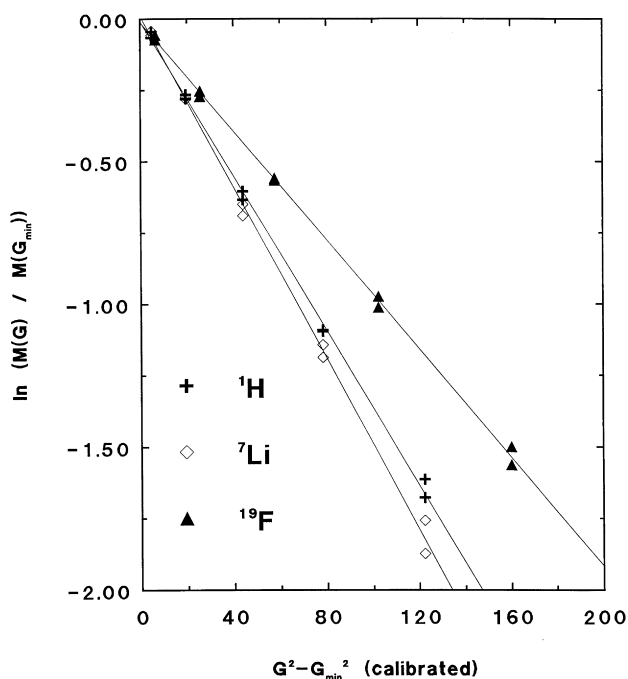For the NMR measurements, pieces of the gel electrolytes

Fig. 2. Representative plots of $\ln\{M(G)/M(G_{\min})\}$ against $(G^2 - G_{\min}^2)$ for a PVDF/DMF/LiT gel (see text for details of salt concentration and temperature).

were placed in 7 mm diameter NMR tubes which were then heated until the gel melted; upon cooling a void-free, homogeneous gel electrolyte sample was obtained.

The gel electrolytes reported in this article each contained 30% PVDF by weight with respect to the solvent alone (irrespective of the salt concentration). The salt concentrations with respect to the solvent are O:Li = 3:1, 6:1 and 15:1 for the PVDF/DMF/LiT gel electrolytes and O:Li = 12:1 and 18:1 for the PVDF/TG/LiT gels.

2.2. Proton NMR spin-echo measurements of transverse relaxation time, T_2

A Carr–Purcell–Meiboom–Gill pulse sequence [8], which takes the form

$$(\pi/2)(+x) - \tau - [\pi(+y) - 2\tau]_n$$

has been used to monitor the proton NMR transverse relaxation in PVDF gel electrolytes and their incorporated liquid electrolytes. Following the initial $(\pi/2)(+x)$ rf pulse, $\pi(+y)$ rf pulses are applied at times τ, 3τ, 5τ,..., which results in the formation of spin-echoes at times 2τ, 4τ, 6τ,..., with magnitude, $M(t)$. Transverse relaxation times, T_2, are obtained by fitting the decay of $M(t)$ to single and bi-exponential functions for liquid and gel electrolytes, respectively.

Each of the proton transverse relaxation measurements were taken at 35°C using a MARAN benchtop pulse NMR analyser, manufactured by Resonance Instruments Ltd., UK, operating at 20 MHz.

2.3. Pulsed field gradient spin-echo NMR measurements of self-diffusion coefficients

Self-diffusion coefficients for solvent molecules, Li^+ cations and $CF_3SO_3^-$ anions in polymer gel electrolytes were determined separately by use of the PFG spin-echo NMR technique [9], applied to ^1H, ^7Li and ^{19}F nuclei, respectively. Each diffusion measurement was obtained using an extensively modified Brüker SXP-100 spectrometer, operating at 100.5 MHz for protons, 95.6 MHz for ^{19}F and 39.1 MHz for ^7Li, with the aid of a commercially available pulse programmer/data acquisition system run from a PC.

In each PFG NMR experiment, the spin-echo is formed at time 2τ by the application of a $(\pi/2)(+x)$ rf pulse at time zero, followed by a $\pi(+y)$ rf pulse at time τ. The amplitude of the spin-echo is attenuated by adding two identical, square shaped, intense magnetic field gradient pulses of duration δ and magnitude $+G$ to the spin-echo pulse sequence. The first gradient pulse, applied between the rf pulses, has the effect of rapidly dephasing the spins, while the second gradient pulse, applied following the $\pi(+y)$ rf pulse at a time Δ after the first, undoes the dephasing effect of the first gradient pulse. The echo amplitude is attenuated by an amount that is dependent on how much the position of the spins has changed by the process of self-diffusion in the
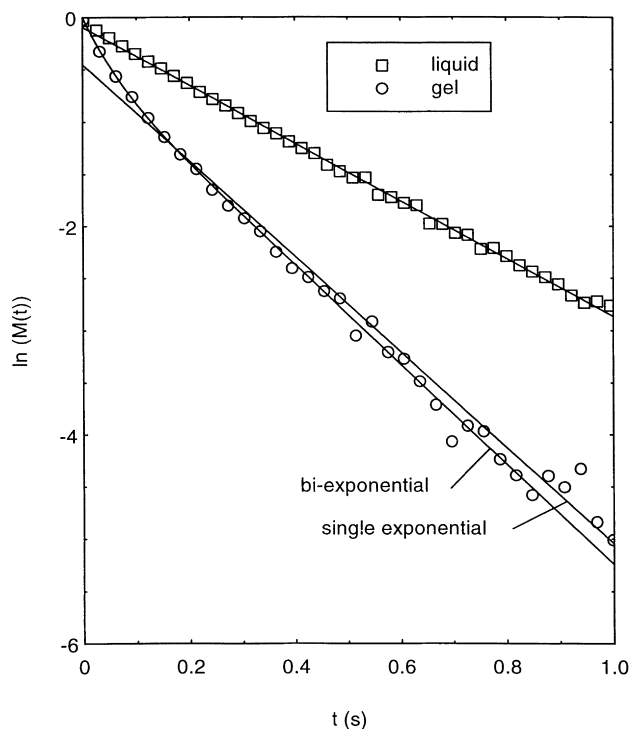
Fig. 3. Plot of $M(t)$ against time for a Carr–Purcell–Meiboom–Gill NMR pulse sequence for a DMF/LiT liquid electrolyte and a 30 wt.% PVDF/DMF/LiT gel electrolyte, each at a salt concentration of O:Li = 3:1.

time interval Δ. It is found that the unattenuated spin-echoes are more stable if a very small field gradient pulse, G_{min}, is applied, rather than no field gradient at all. In this case, the attenuation of the spin-echo is given by

$$\ln\left\{\frac{M(G)}{M(G_{min})}\right\} = -\gamma^2\delta^2 D(G^2 - G_{min}^2)\left(\Delta - \frac{\delta}{3}\right), \qquad (1)$$

where D is the self-diffusion coefficient, $M(G)$ is the magnitude of the spin-echo in the presence of gradient pulses of magnitude $+ G$, and $M(G_{min})$ is the magnitude of the 'unattenuated' spin-echo. The gradient coils were calibrated on a sample of distilled water using the diffusion data reported by Mills [10] and could deliver a maximum field gradient of $2\,\mathrm{T\,m^{-1}}$ to an accuracy of 1 part in 4096.

As we have previously reported for liquid electrolytes [1,2], the diffusion coefficients were determined by measuring the intensity of the spin-echoes with a number of different values of magnetic field gradient applied. Representative plots of $\ln(M(G)/M(G_{min}))$ against $(G^2 - G_{min}^2)$ for protons and fluorine in a PVDF/DMF/LiT gel at a salt concentration of 15:1 and a temperature of 55°C are shown in Fig. 1, with equivalent plots for a gel with a salt concentration of 3:1 at 55°C are shown in Fig. 2. In Fig. 2 the data for lithium in a PVDF/DMF/LiT gel with a salt concentration of 15:1 at 75°C is also given. In each case the echo attenuation was seen to decay exponentially with $(G^2 - G_{min}^2)$, indicating the observation of a single self-diffusion coefficient for each species.

In all PFG NMR experiments a gradient pulse width of

$\delta = 3$ ms, a gradient pulse separation of $\Delta = 40$ ms and $\tau = 30$ ms was used. For the ^{1}H and ^{19}F measurements, where a contribution to the bulk magnetisation arises from the PVDF molecules, it was found that by using these parameters in the diffusion experiments, a single diffusion coefficient was obtained, relating to the solvent and triflate ion diffusion respectively, as the magnetisation arising from the PVDF had significantly decayed by the time of the spin-echo due to the shorter transverse relaxation time of proton and fluorine nuclei in PVDF.

For each gel electrolyte system investigated, diffusion measurements were taken at 10°C intervals in the temperature range 35 to 75°C. At each of these temperatures the electrolytes remained in a 'gelled' state (i.e. they had not melted). The range of salt concentrations were limited to those where the NMR signal intensity allowed measurements of the diffusion coefficient of all three nuclei to be determined, namely concentrations above 15:1 for PVDF/DMF/LiT gel electrolytes and above 18:1 for PVDF/TG/LiT gel electrolytes. In general, the experimental uncertainty in the proton diffusion coefficients was better than 3%, with uncertainties of 5–10% being estimated for the lithium and fluorine diffusion measurements.

2.4. Ionic conductivity measurements

Bulk ionic conductivities were measured using a Solartron SI 1260 impedance/gain-phase analyser in the frequency range 1 Hz to 400 kHz. The gel electrolytes were melt cast between two stainless steel blocking electrodes, ensuring that good contact was made at both electrode–electrolyte interfaces. In all cases the contact area was 1 cm^2 and a constant thickness in the range 0.3–2.0 mm was maintained using a PTFE spacer [6].

3. Results and discussion

3.1. Measurements of proton NMR transverse relaxation time T_2

Proton T_2 measurements were undertaken on the PVDF gel electrolytes and on the corresponding DMF/LiT and TG/LiT liquid electrolytes. Fig. 3 compares the decay of the echo height $M(t)$ for a DMF/LiT liquid electrolyte with that for a 30 wt.% PVDF/DMF/LiT gel electrolyte, each salted to a concentration of O:Li = 3:1. The decay of $M(t)$ for the liquid electrolyte is well described by a single exponential decay, with T_2 taking a value of 348 ms. However, a comparison of single and bi-exponential fits to $M(t)$ for the gel electrolyte, shown in Fig. 3, indicates that $M(t)$ is much better described by a bi-exponential decay. The slower decaying component of this bi-exponential, which takes a T_2 value of 209 ms and accounts for 64% of the decay, arises from the protons within the gel with the greatest mobility and is assigned to the protons associated with the liquid electrolyte component of DMF molecules. The faster
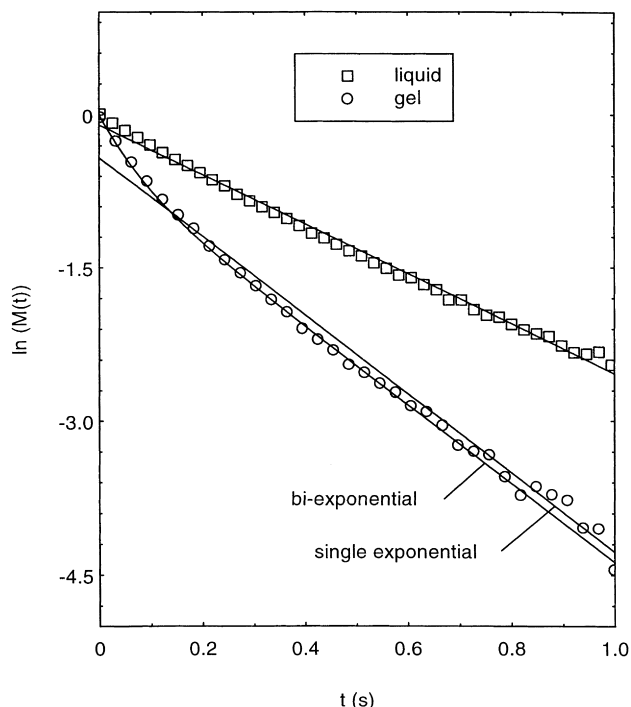
Fig. 4. Plot of *M(t)* against time for a Carr–Purcell–Meiboom–Gill NMR pulse sequence for a TG/LiT liquid electrolyte and a 30 wt.% PVDF/TG/LiT gel electrolyte, each at a salt concentration of O:Li = 12:1.
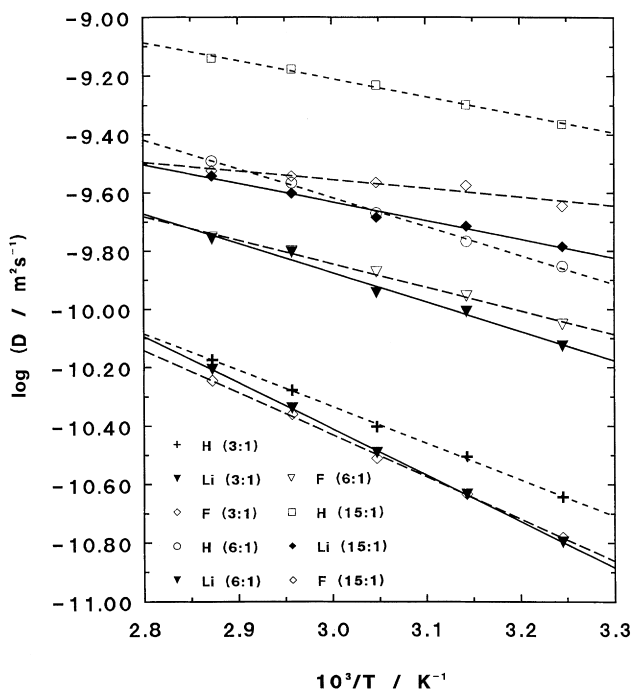

Fig. 5. Arrhenius plot of proton, lithium and fluorine diffusion coefficients for PVDF/DMF/LiT gel electrolytes. The solid lines represent the best fit lines of the data to the Arrhenius equation.
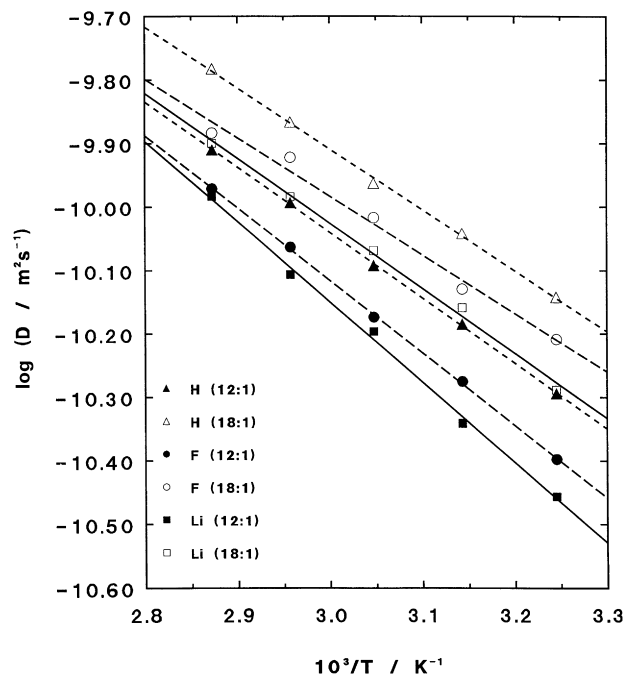

Fig. 6. Arrhenius plot of proton, lithium and fluorine diffusion coefficients for PVDF/TG/LiT gel electrolytes. The solid lines represent the best fit lines of the data to the Arrhenius equation.

decaying component, with a T_2 value of 48 ms, is due to protons that are less mobile within a gel rich phase which includes both DMF solvent and PVDF molecules. On the basis of the initial concentration of the solvent in the gel–solvent–salt mixture, the proportion of protons in the slowly decaying component (64%) is less than expected if all the solvent molecules (∼ 85%) contributed to the decay. This discrepancy can be accounted for by allowing a solvation sheath around those amorphous parts of the PVDF that are not intimately involved with the formation of PVDF crystallite junctions. A simple model of such a partial solvation sheath indicates that the proportion of free mobile solvent is typically about twice that which is "immobilised" in the solvation sheath for an observed slow decay component of 64%.

Similar results have been obtained for TG based gel and liquid electrolytes, salted to a concentration of O:Li = 12:1 and these are shown in Fig. 4. In this case, T_2 for the liquid electrolyte takes a value of 389 ms, while the T_2 values obtained from the bi-exponential fit to *M(t)* are 261 and 61 ms for the slow and fast decaying components respectively, with a slow decaying fraction of 60%.

Previous studies [6,7] have shown these PVDF gels to be partially crystalline. The contribution to the decay of *M(t)* from the crystalline regions, including any interlamella unsolvated amorphous PVDF, is expected to be of a timescale orders of magnitude shorter than shown in the results in Figs. 3 and 4. Studies are to be undertaken to confirm this.

These results demonstrate that the gel electrolytes contain a liquid-like phase which is very similar to that in the

Table 1
Values of activation energy for diffusion in (a) PVDF/DMF/LiT gel electrolytes; (b) DMF/LiT liquid electrolytes

O:Li	Proton E_D (kJ mol^{-1})	Fluorine E_D (kJ mol^{-1})	Lithium E_D (kJ mol^{-1})
(a)			
3:1	23.9 ± 0.5	27.6 ± 0.6	30.3 ± 0.3
6:1	19.0 ± 0.6	15.5 ± 0.3	19.3 ± 1.5
15:1	11.8 ± 0.5	5.7 ± 1.1	12.2 ± 1.0
(b)			
3:1	27.0 ± 0.3	28.7 ± 0.5	29.1 ± 0.8
6:1	17.2 ± 0.3	16.5 ± 0.2	18.1 ± 0.5
15:1	13.2 ± 0.2	12.0 ± 0.4	14.0 ± 0.4

Table 2
Values of activation energy for diffusion in (a) PVDF/TG/LiT gel electrolytes; (b) TG/LiT liquid electrolytes

O:Li	Proton E_D (kJ mol^{-1})	Fluorine E_D (kJ mol^{-1})	Lithium E_D (kJ mol^{-1})
(a)			
12:1	19.7 ± 0.2	21.9 ± 0.3	24.2 ± 0.8
18:1	18.4 ± 0.4	17.7 ± 1.2	19.6 ± 0.7
(b)			
12:1	24.0 ± 0.2	25.0 ± 0.3	27.0 ± 1.1
18:1	21.5 ± 0.2	21.9 ± 0.4	21.2 ± 0.6

corresponding liquid electrolyte and confirm that the PFG spin-echo measurements to be reported refer to the liquid electrolyte phase in the gel electrolyte. It can therefore be anticipated, as will be shown, that the results for the self diffusion coefficients of the solvent molecules and the ions in the gel electrolytes are very similar to those previously obtained for the corresponding liquid electrolytes [1,2]. There are, however, small but significant differences which will be discussed.

3.2. Proton, ^{7}Li and ^{19}F self diffusion measurements

Figs. 5 and 6 show the variation with temperature of the self diffusion coefficients for the protons, Li$^+$ ions and CF$_3$SO$_3^-$ ions in the PVDF/DMF/LiT and PVDF/TG/LiT gel electrolytes at selected salt concentrations.

A similar pattern of behaviour is observed for both the polar solvent DMF and the less polar solvent TG. First, the diffusion coefficients for the solvent molecules are always greater than for the Li$^+$ and CF$_3$SO$_3^-$ ions. This is exactly the same as the behaviour observed previously for the liquid electrolytes [1,2]. It is attributed to the fact that the proton signal is predominantly arising from the free solvent molecules not solvating the salt, at least in the time scale of the NMR experiment (~40 ms).

Secondly, the diffusion coefficients of the cation and the anion are very similar, with the fluorine values slightly greater than the lithium values at lower salt concentrations and virtually identical at the highest salt concentrations. This could be due either to increasing ionic association so that ion pairs are being observed where the Li$^+$ and CF$_3$SO$_3^-$ ions move as single species, or to correlated motion of the ions as suggested previously for LiT/polyethylene glycol electrolytes [11–13].

It is also clear from Figs. 5 and 6 that it is realistic to fit the temperature dependence of self diffusion for all species to the Arrhenius equation

$$D = D_0 \exp\left[\frac{-E_D}{RT} \right]. \qquad (2)$$

As was observed for the liquid electrolytes [1,2], the value of D_0 increases with increasing salt concentration

for each nucleus. The activation energies for the diffusion of each nucleus also increases with increasing salt concentration reflecting the increased interactions, which leads to the increased energy barrier that must be overcome for the process of diffusion to occur. At each salt concentration the activation energy for lithium diffusion is greater than that for either proton or fluorine diffusion, reflecting stronger interactions involving lithium ions than either triflate ions or the solvent molecules in the gel electrolytes.

It is instructive to compare the values of activation energy for the diffusion of the different species in the gel electrolytes with those in the corresponding liquid electrolytes. These results are shown in Table 1 for the DMF based electrolytes. It can be seen that, in general, there is very reasonable agreement in the activation energies for diffusion of all species in the gel and liquid electrolytes. Moreover, the 'ranking' of activation energies for the diffusion of protons, lithium and fluorine nuclei at each salt concentration in the liquid electrolytes is precisely that found for the gel electrolytes, although it should be noted that at each salt concentration the activation energies for the diffusion of different species in liquid electrolytes are much more closely matched than for the corresponding gel electrolytes.

These similarities in the activation energies for diffusion of species in liquid and gel electrolytes appear to indicate that similarities exist between the mechanisms for diffusion in liquid and gel electrolytes. It would seem likely, therefore, that regions of DMF/LiT liquid electrolyte do exist within PVDF gel electrolytes.

A comparison of the activation energies for diffusion in the PVDF/TG/LiT gel electrolytes and the TG/LiT liquid electrolytes is presented in Table 2. In this case, it can be seen that the activation energy for the diffusion of all the species at both salt concentrations is slightly greater (by about 2–4 kJ mol^{-1}) for the liquid electrolytes than for the gel electrolytes. This may be due to the presence of PVDF, with its higher dielectric constant than that of TG, increasing the overall dielectric constant of the electrolyte system, with the result being lower activation energies for the diffusion of each species. Alternatively, the lower activation energies in the gel electrolytes could be an indication that interactions between species in the liquid electrolytes and the PVDF matrix are occurring which leads to slightly less
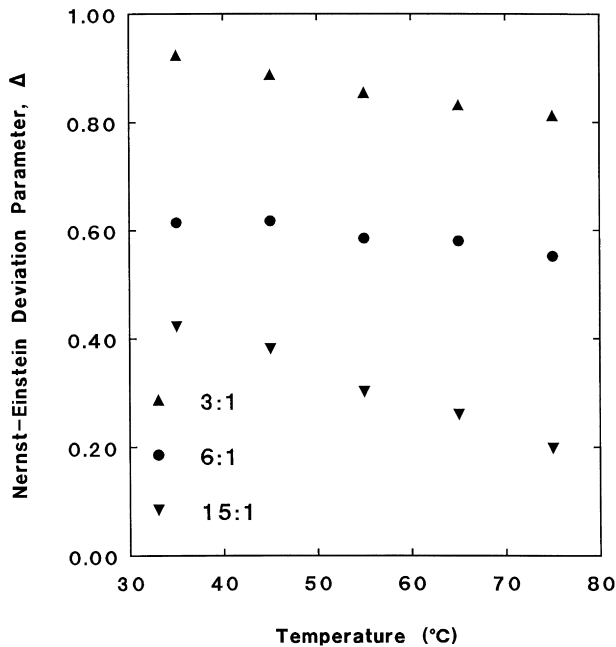
Fig. 7. Behaviour of the Nernst–Einstein deviation parameter with salt concentration and temperature for PVDF/DMF/LiT gel electrolytes.

energy being required to initiate the diffusion mechanism for each species.

3.3. Ionic association: use of Nernst–Einstein equation

For fully dissociated ions, the Nernst–Einstein equation can be used to give a calculated value of the ionic conductivity, σ_{calc}, from the diffusion coefficients of the cation and
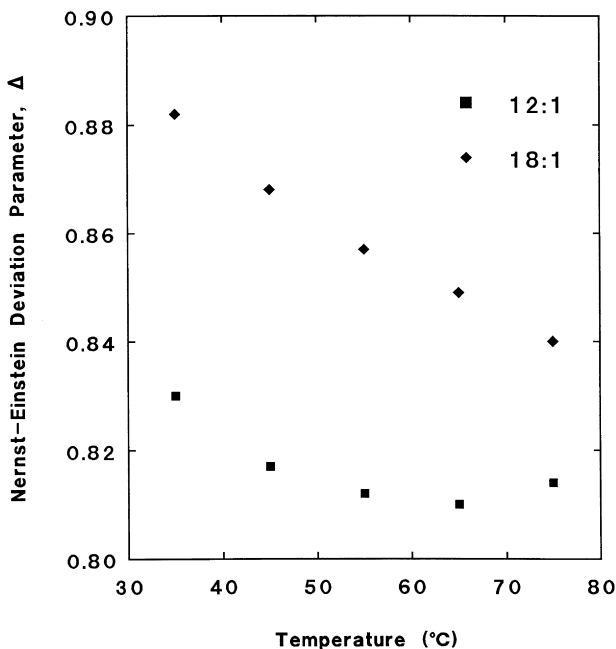

Fig. 8. Behaviour of the Nernst–Einstein deviation parameter with salt concentration and temperature for PVDF/TG/LiT gel electrolytes.
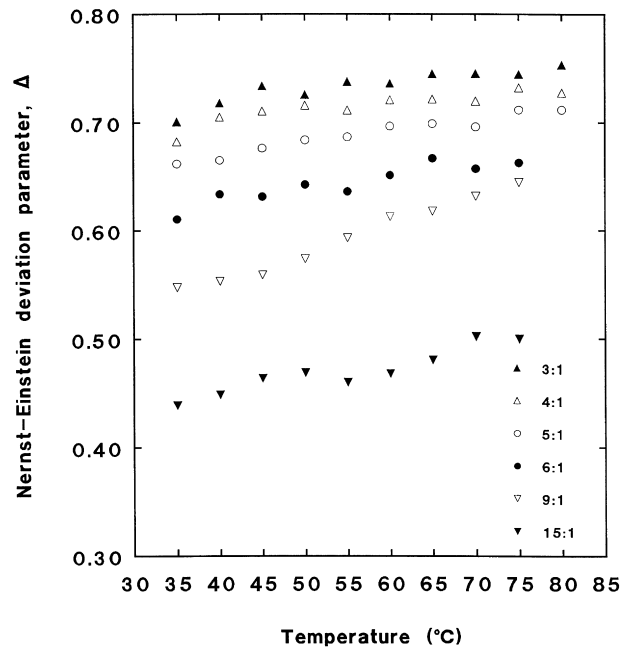

Fig. 9. Behaviour of the Nernst–Einstein deviation parameter with salt concentration and temperature for DMF/LiT liquid electrolytes.

anion ($D(Li^+)$ and $D(CF_3SO_3^-)$) as

$$\sigma_{calc} = \frac{nq^2}{kT}[D(Li^+) + D(CF_3SO_3^-)], \qquad (3)$$

where n is the number of anions and/or cations per unit volume of solution and q is the charge on each ion.

Generally calculated values σ_{calc} are greater than those measured directly, σ_{meas} due to ionic association [1,2]. This can be caused by the formation of discrete ion pairs, higher ion aggregates or correlated motion of ions which results in currentless diffusion and contributes to the diffusion measurements, but not to the conductivity measurements. A quantitative measure of ionic association is given by the calculation of the quantity Δ from the relation

$$\sigma_{meas} = \sigma_{calc}(1 - \Delta). \qquad (4)$$

Values of Δ as a function of salt concentration and temperature are shown in Figs. 7 and 8 for the PVDF/DMF/LiT and the PVDF/TG/LiT gel electrolytes, respectively. In the PVDF/DMF/LiT gel electrolytes, Δ, and therefore the degree of ionic association, increases with increasing salt concentration similar to that observed for the DMF/LiT liquid electrolytes, but for this system, Δ increases more sharply with salt concentration in the gels than in the liquid electrolytes.

In the case of the PVDF/TG/LiT gel electrolytes, the behaviour with salt concentration is identical to that found for the corresponding liquid electrolytes, with a decrease in Δ with increasing salt concentration consistent with increasing ionic melt-like behaviour, in which small amounts of solvent disrupts the symmetrical charge field and increases the correlated motion of the ions [1,2,12,13].
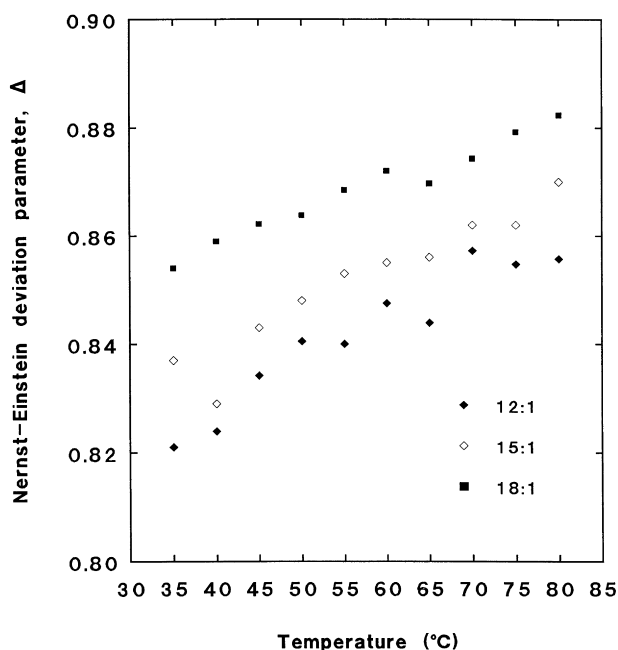
Fig. 10. Behaviour of the Nernst–Einstein deviation parameter with salt concentration and temperature for TG/LiT liquid electrolytes.

electrolytes [6,7], showed that the overall crystalline content of the gels were identical whether lithium triflate was present or not, but indicated that the dimensions of the crystalline regions were significantly smaller in the presence of lithium triflate, because the salt had the effect of nucleating crystalline regions. Any ions contained within a crystalline region of the gel would be unlikely to contribute to the ionic conductivity but those near the periphery may be released into the regions of liquid electrolyte as the temperature increases.

An alternative explanation may be provided if we allow an exchange of solvent molecules (or salt ions) associated with the solvation sheath with those in the free solvent phase. This would lead to a decrease in the mean displacement of the diffusing species in the free solvent component as it exchanged with species in the solvation sheath, and hence to a reduced diffusion coefficient of the free solvent. In addition, the release of solvent molecules from the solvation sheath results in a low apparent diffusion coefficient for the viscous part. Both effects combine resulting in an overall decrease in the measured diffusion coefficient. This process of exchange increases with temperature lowering σ_{calc} compared to the liquid electrolytes and resulting in a fall in Δ with temperature.

In each of these cases, the results show that the PVDF does interact with the solvent electrolyte in these gels and affects the conductivity over and above the presence of the PVDF simply increasing the tortuosity for ionic diffusion.

A direct comparison of values of Δ for the PVDF/TG/LiT gel and liquid electrolytes (Figs. 7 and 9) show them to be very similar. For the DMF based liquid and gel electrolytes (Figs. 8 and 10) the correspondence is not nearly so close, with a greater spread of Δ values with salt concentration for the PVDF/DMF//LiT gel electrolytes.

However, for both the DMF and tetraglyme systems, the decrease of Δ with temperature in the gel electrolytes is precisely the opposite to that found for the liquid electrolytes as shown by comparing Fig. 7 with Fig. 9 for DMF and Fig. 8 with Fig. 10 for tetraglyme. The increase in ionic association with temperature in liquid electrolyte systems is well established [1,13,14] and is consistent with Raman studies of ion pairing [16,17]. The fall in the value of Δ and hence the level of ionic association, with increasing temperature for the gel electrolytes, could be due either to the release of ions from crystalline regions of the gel into regions of liquid electrolyte or to the precipitation of neutral associated species onto PVDF regions increasing the proportion of dissociated ions in the liquid electrolyte component.

Previous X-ray and DSC studies on PVDF/TG/LiT gel

3.4. Comparison of diffusion and ionic conductivity measurements on gel electrolytes with those on the corresponding liquid electrolytes

It has been shown previously that the PVDF gel electrolytes show a reduction in the ionic conductivity compared with the corresponding liquid electrolytes by an amount which is dependent on temperature, the proportion of PVDF and, in some cases, the salt concentration [14,15]. Whilst the similarity of the temperature dependence suggested that the presence of PVDF simply reduced the rates of transport of ions because of an increase in the tortuosity for ionic diffusion, the existence of polymer salt interactions could not be ruled out.

In Table 3, comparisons are shown for the diffusion coefficients and the ionic conductivities of gel and liquid electrolytes based on DMF. First, it can be seen from Table 3 (comparison of the ionic conductivity) that with the exception of high salt concentration at low temperature, the ratio of the ionic conductivity of the gel to that of the corresponding liquid electrolyte is independent of salt

Table 3
Comparison of (a) the diffusion of species; (b) the ionic conductivity in PVDF/DMF/LiT gel electrolytes and DMF/LiT liquid electrolytes

	D_{gel}/D_{liquid} (35°C)			D_{gel}/D_{liquid} (75°C)		
(a)						
O:Li	^{1}H	^{19}F	^{7}Li	^{1}H	^{19}F	^{7}Li
3:1	0.52	0.64	0.64	0.45	0.59	0.63
6:1	0.48	0.41	0.45	0.51	0.38	0.46
15:1	0.46	0.36	0.39	0.43	0.27	0.37
(b)						
O:Li	$\sigma_{gel}/\sigma_{liquid}$ (35°C)			$\sigma_{gel}/\sigma_{liquid}$ (75°C)		
3:1	0.16			0.45		
6:1	0.42			0.58		
15:1	0.38			0.52		

Table 4
Comparison of (a) the diffusion of species; (b) the ionic conductivity in PVDF/TG/LiT gel electrolytes and TG/LiT liquid electrolytes

	D_{gel}/D_{liquid} (35°C)			D_{gel}/D_{liquid} (75°C)		
(a)						
O:Li	^{1}H	^{19}F	^{7}Li	^{1}H	^{19}F	^{7}Li
12:1	0.53	0.69	0.74	0.44	0.54	0.63
18:1	0.46	0.69	0.67	0.40	0.55	0.60
(b)						
O:Li	$\sigma_{gel}/\sigma_{liquid}$ (35°C)			$\sigma_{gel}/\sigma_{liquid}$ (75°C)		
12:1	0.67			0.78		
18:1	0.55			0.83		

concentration and this has been shown previously to hold for a wider range of salt concentrations than those studied here. A large transition occurs in the conductivity of the 3:1 gel and is probably due to the LiT salt precipitating out of the electrolyte solution in the gel.

Turning to the diffusion coefficients, the results in Table 3 (comparison of the diffusion of the species) show that the fractional reduction in proton diffusion coefficient upon the addition of PVDF to the liquid electrolytes remains relatively constant with increasing salt concentration, taking a value of approximately 50% of the proton diffusion coefficient of the corresponding liquid electrolyte. In contrast, D_{gel}/D_{liquid} for fluorine and lithium at the same temperature are closely mirrored by each other and are found to decrease as the salt concentration decreases.

As it has only been possible to investigate PVDF/TG/LiT gel electrolytes at two salt concentrations via the PFG NMR technique, with these electrolytes showing very similar behaviour, the corresponding comparisons of diffusion coefficients and ionic conductivities (Table 4) for the gel and liquid electrolytes based on tetraglyme with respect to salt concentration, is less meaningful.

However, for both the DMF and tetraglyme systems, the observed increase in $\sigma_{gel}/\sigma_{liquid}$ with increasing temperature is in line with the observed decrease in ionic association Δ with temperature for the gels which contrasts with the increase in Δ for the liquid electrolytes; together these trends more than compensate for any decrease in D_{gel}/D_{liquid} for fluorine and lithium with increasing temperature.

4. Conclusions

The technique of PFG NMR has been used to measure the diffusion coefficients of protons, fluorine and lithium nuclei in PVDF/DMF/LiT and PVDF/TG/LiT gel electrolytes containing 30% PVDF by weight with respect to the solvent. Proton diffusion coefficients in the range $(2.28–72.6) \times 10^{-11}$ m^2 s^{-1} for the PVDF/DMF/LiT electrolytes and $(5.08–16.5) \times 10^{-11}$ m^2 s^{-1} for the PVDF/TG/LiT electrolytes were obtained, with higher diffusion coefficients being measured at low salt concentrations and high temperatures. The predominant overall effect of the PVDF gels is to

reduce the ionic conductivities and the diffusion coefficients of solvent molecules, to about half of that of the corresponding liquid electrolytes. The gel:liquid ratio for fluorine and lithium diffusion in both the systems are in reasonable agreement with each other at any given salt concentration and temperature, but are, in general, different to the ratio for proton diffusion.

The similarities in the behaviour of the liquid and gel systems are greater than the differences: the proton diffusion coefficient is greater than that for fluorine and lithium in both liquid and gel electrolytes; the temperature dependence of the diffusion is Arrhenius with similar activation energies in the gel and liquid systems; and the degree of ionic association Δ and the variation with salt concentration is similar for the liquids compared to the gels. It appears that the overall mechanism for diffusion and conduction are the same in the gel and liquid electrolytes and supports the view that the gel electrolyte behaviour is predominantly determined by the liquid electrolyte component, consistent with the picture from the T_2 measurements of regions of liquid electrolyte within the gel electrolyte framework.

However there are clear differences in the behaviour of the gels compared with the liquid electrolytes: the lower activation energies for the diffusion of each species in the tetraglyme gel electrolytes compared with the corresponding liquids; the greater range of the ionic association parameter Δ and sharper increase with salt concentration for the PVDF/DMF/LiT gel electrolytes compared to the corresponding liquid electrolytes; and most strikingly, the decrease in ionic association with temperature for PVDF gel electrolytes is in marked contrast to the increase in the liquid electrolytes previously observed. This is a strong evidence to suggest that the PVDF in some way interacts with the liquid electrolyte component to modify the properties of the gel electrolytes.

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