

# FTIR–ATR studies of diffusion and perturbation of water in polyelectrolyte thin films. Part 4. Diffusion, perturbation and swelling processes for ionic solutions in SPEES/PES membranes

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## Abstract

We report diffusion rates and equilibrium concentrations of water in a polyelectrolyte SPEES/PES film using ATR/FTIR spectroscopy. The data for water obtained by fitting spectral intensities to a dual mode diffusion model in the presence of different counter ions (at 0.2 mol dm<sup>-3</sup>) follow the order Li<sup>+</sup> > Cs<sup>+</sup> > Na<sup>+</sup> > Ca<sup>2+</sup> > K<sup>+</sup>. Diffusion is progressively slower for higher concentrations of NaCl (0.2–0.85 mol dm<sup>-3</sup>) and the NO<sub>3</sub><sup>-</sup> counter anion leads to a faster diffusion rate than for Cl<sup>-</sup> at the same concentration. Both water uptake and diffusion rates are broadly consistent with expectations based on the differential degrees of swelling, caused by changes in the SO<sub>3</sub><sup>-</sup>/SO<sub>3</sub><sup>-</sup> interpolymer chain repulsive forces leading to a decrease in volume diffusion compared with the value for pure water. Direct spectral measurements of the degree of swelling confirm that the process does occur, although the order of the swelling amounts does not map directly onto that of the diffusion rates. This is probably because the interfacial dissociation processes are hydration dependent. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Polyelectrolytes; SPEES/PES; Diffusion

## 1. Introduction and background

Extensive studies [1–10] have been made over the last two decades of the swelling processes (volume transitions) in polyelectrolyte membranes in relation to their application in industry as separation membranes, as sensors and actuators, and for their extensive use in drug encapsulation and delivery [11–13]. A wide range of polyelectrolyte membranes have been studied, both in the absence and in the presence of electrolyte solutions with the aim of characterising [1–8,14,17] and modelling [5,7,11,15–17,23] the behaviour of the polymeric molecules in different aqueous environments in order to understand membrane permeability at molecular level. However, relatively few measurements have been made on the diffusion of liquid water into such membranes [18–22], despite the fact that such measurements give a direct measure of the permeability of the most important small molecule (H<sub>2</sub>O) that comes into contact (in the real world) with such membranes. The

principal object of this paper is to use measurements of water diffusion from polyelectrolyte solutions in polyether-sulfone SPEES/PES membranes to show how the permeability process can be correlated with swelling processes, understood in terms of the shielded repulsion between polymer chains, as a function of electrolyte type, ionic charge and concentration. We demonstrate how a knowledge of the swelling process can be used to predict the rate of diffusion and therefore the permeability of such polymer films.

The diffusion of water in thin SPEES/PES films was measured in the same way as that reported previously [20,21]. Details of the cell used for ATR–FTIR measurements is given in Section 2 and in our previous work. The measurements were interpreted using the dual mode model [21,24–27] for diffusion of small molecules into polymers. Again, the necessary analytical details are given in our previous papers [20,21]. The model uses two diffusion coefficients,  $D_1$  and  $D_2$ , and weighting factors  $x_n$ , which measure the relative proportions of the two Fickian processes which are included in the model, see Eqs. (1) and (2). The FTIR–ATR method provides a unique in situ method of direct identification and quantification of

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concentration of water in a polymeric membrane and, in addition, provides information about the diffusion of the perturbation of water at any particular point in time. The technique was developed by Fieldson and Barbari [19], and has been demonstrated previously for the study of water diffusing in Nafion polymers [18,22] and polyethersulfones [20,21]. It has also been used to study the diffusion of other small molecules [28] in polymeric systems. The two diffusion coefficients, although strictly numerical parameters [20] which arise from the combination of two *parallel Fickian diffusion processes*, are nevertheless expected to correspond approximately to the water sorption at the aqueous/polymer interface and the diffusion of the water into the ‘voids’ in bulk of the polymer matrix. The water is considered to be partially mobile in both processes [27]. Application of the model results in two equations for these first and second diffusional modes, respectively. The total absorbance, measured from the infrared spectrum can be deduced by the addition of  $A_1$  and  $A_2$  after rearrangement of Eqs. (1) and (2).

$$\frac{A_1 - x_1 A_0}{x_1 (A_\infty - A_0)} = 1 - \frac{8\gamma}{\pi[1 - \exp(-2\gamma L)]} \sum_{n=0}^{\infty} \left\{ \frac{\exp\left(\frac{-D_1(2n+1)^2\pi^2 t}{4L^2}\right) \left[ \frac{(2n+1)\pi}{2L} \exp(-2\gamma L) + (-1)^n(2\gamma) \right]}{(2n+1) \left[ 4\gamma^2 + \left(\frac{(2n+1)\pi}{2L}\right)^2 \right]} \right\} \quad (1)$$

$$\frac{A_2 - x_2 A_0}{x_2 (A_\infty - A_0)} = 1 - \frac{8\gamma}{\pi[1 - \exp(-2\gamma L)]} \sum_{n=0}^{\infty} \left\{ \frac{\exp\left(\frac{-D_2(2n+1)^2\pi^2 t}{4L^2}\right) \left[ \frac{(2n+1)\pi}{2L} \exp(-2\gamma L) + (-1)^n(2\gamma) \right]}{(2n+1) \left[ 4\gamma^2 + \left(\frac{(2n+1)\pi}{2L}\right)^2 \right]} \right\} \quad (2)$$

$A$  is the infrared (ATR) absorbance (at time  $t$ ),  $L$  is the film thickness and  $\gamma$  is the inverse penetration depth in the ATR experiment [19–21].  $A_\infty$  (at equilibrium) was determined by allowing the experiment to reach saturation levels of water as determined from the spectrum. The parameters  $D_1$  and  $D_2$  and  $x_1$  were calculated using the Levenberg–Marquardt non-linear least-squares fitting procedure [29,30] described previously.

## 2. Experimental

### 2.1. Chemicals

SPEES/PES with the following structure, was obtained from NWW Acumem Limited and used as received.

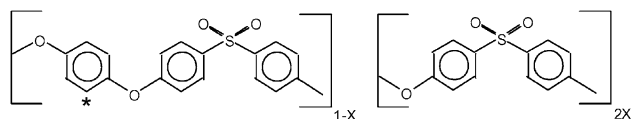


Table 1

The characteristic of copolymers which were used in this work are summarised below

	$2x/1-x$	Exchange capacity (Eqv kg <sup>-1</sup> )	Water uptake (%)
S <sub>20</sub>	9	0.398	5
S <sub>8</sub>	3	0.894	12.7
S <sub>5</sub>	1.5	1.297	20.5

The copolymer is sulphonated only at hydroquinone residue \* so that ion exchange capacity of sulphonated polymer is pre-determined by copolymer composition. Sulphonation occurs in 98% H<sub>2</sub>SO<sub>4</sub> without degradation.

Degree of sulphonation is characterised by ‘S–No’, where

$$S = \frac{\text{No. of non-sulphonatable rings}}{\text{No. of sulphonatable rings}} = (2 + 2x)/(1 - x)$$

Most of the measurements reported here were made on S8

material which has a 12.7% water uptake capacity (see Table 1). All the solid salts (chloride and nitrate) were 99 + % purity and the solvents, 1-methyl-2-pyrrolidone, NMP (99 + %, HPLC grade), and dimethylformamide, DMF (99.9 + %, HPLC grade) were obtained from Aldrich Chemical Company. Deionised water (Millipore) was used throughout.

### 2.2. Sample preparation and spectroscopic measurements

The ATR crystals used in the experiments were polished 45° ZnSe parallelepipeds (50 × 10 × 6 mm<sup>3</sup>), obtained from Graseby Specac Ltd. Before each experiment, the crystals were cleaned by washing with acetone and methanol and then by refluxing in hot 2-propanol for at least 4 h. The SPEES/PES polymer films were cast onto ZnSe substrates from 7% SPEES/PES in NMP. The films were cured at 65 °C for 24 h. The thickness of each film was determined to be 10 μm (±5%) using a surface profiler (Laser Form Talysurf). Salt solutions were made up by weight immediately prior to use. FTIR measurements were made by averaging two scans on a Mattson Polaris instrument, operating

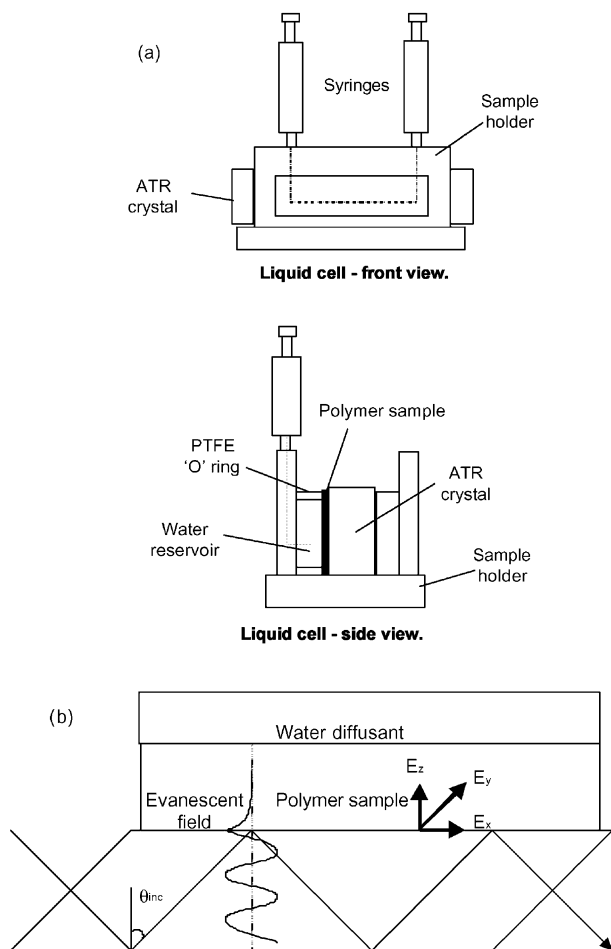


Fig. 1. (a) FTIR-ATR flow through liquid cell used in this work. (b) ATR-optical configuration for the water/polymer interface.

at  $4\text{ cm}^{-1}$  resolution, and fitted with a liquid nitrogen-cooled mercury-cadmium-telluride detector (MCT).

The film-coated crystal was mounted in a flow-through ATR cell (Graseby Specac Ltd) is shown in Fig. 1. The solvent (water,  $25\text{ }^\circ\text{C}$ ) was injected from one side of the cell and the excess of solvent was collected in a reservoir at the other side of the cell. A background spectrum of the dried film was taken as a reference. The subsequent sample spectra for diffusion measurements were then obtained using a 'macro' program. In a diffusion experiment, it should be noted that the experimental data were not taken at one particular time, but over the sampling period (in this case two scans (13 s)). The mean value of time was used for determining the diffusion coefficients.

### 3. Measurements and data treatment

The diffusion of water into the SPEES/PES films was measured by observing the  $\nu(\text{OH})$  stretching band, Fig. 2, in the presence of a 0.2 M solution of each of the electro-

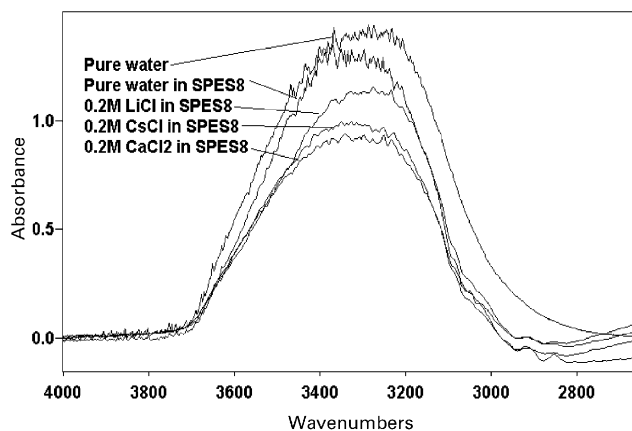


Fig. 2. FTIR spectra as obtained in  $\nu(\text{OH})$  region for water in different aqueous metal chlorides.

lytes studied. This peak was integrated from 2945 to  $3800\text{ cm}^{-1}$  in order to obtain the integrated absorption at each mean time. The integrated intensities as a function of time, are shown in Fig. 3 for the counter cations studied. It is seen that the intensity of the OH band of diffusing water increases rapidly and reached an equilibrium level at about 1000 s. All the measurements for the different cations were made on the SPEES/PES, S8 material, and so the polymer charge density remains the same within this series. Diffusion coefficients obtained by fitting diffusion curves such as those shown in Fig. 3 to Eqs. (1) and (2) are given in Table 2. As indicated earlier,  $D_1$  is probably related to the diffusion process for initial stage of sorption onto the polymer surface, whereas  $D_2$  is related to the diffusion coefficient of partially mobile water molecules through the polymer matrix at longer times. It is clear that there is a significant reduction in the rate of water diffusion at the polymer interface and within the polymer when the electrolyte solution is

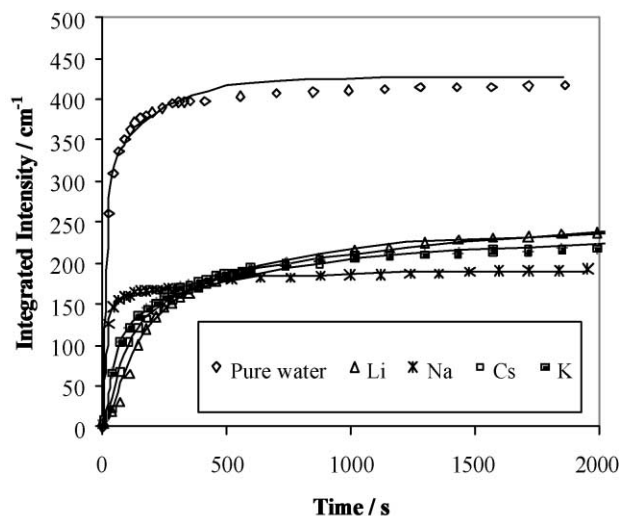


Fig. 3. Comparison of diffusion curves for different cations in aqueous metal chlorides.

Table 2

The dual mode diffusion coefficients and distribution parameter of water molecules into SPEES/PES (S8) in the presence of cations

Ion	$D_1$ ( $\text{cm}^2 \text{s}^{-1}$ )	$D_2$ ( $\text{cm}^2 \text{s}^{-1}$ )	$x_1$
Pure water	$(1.8 \pm 0.3) \times 10^{-8}$	$(2.16 \pm 0.24) \times 10^{-9}$	$0.76 \pm 0.03$
$\text{Li}^+$	$(9.77 \pm 1.0) \times 10^{-9}$	$(15.6 \pm 0.4) \times 10^{-10}$	$0.58 \pm 0.02$
$\text{Na}^+$	$(6.69 \pm 0.8) \times 10^{-9}$	$(5.13 \pm 0.4) \times 10^{-10}$	$0.62 \pm 0.03$
$\text{K}^+$	$(4.27 \pm 0.6) \times 10^{-9}$	$(6.13 \pm 0.5) \times 10^{-10}$	$0.53 \pm 0.03$
$\text{Cs}^+$	$(9.23 \pm 1.0) \times 10^{-9}$	$(7.18 \pm 0.6) \times 10^{-10}$	$0.71 \pm 0.04$
$\text{Ca}^{2+}$	$(6.05 \pm 0.7) \times 10^{-9}$	$(4.89 \pm 0.5) \times 10^{-10}$	$0.51 \pm 0.02$

used in place of the pure water. This is expected from previous work [1–8] since it has been shown that the addition of counter cations to the aqueous ambient in contact with such polymer films results in the shielding of the repulsive forces between the polymer chains and thereby to a reduction in the degree of swelling in the polymer. Since the diffusion of water is expected to depend critically on the microvoids created by the swelling process, the diffusion process would be slowed up as the amount of swelling drops. Relatively little change is observed in the value of  $x_1$  in this series, demonstrating that the relative weightings of the two processes is not severely affected by the presence of a 0.2 M electrolyte solution. Data for the diffusion process of different concentrations of NaCl into the S8 polymer are shown in Fig. 4 and Table 3. Again, as expected, higher ionic concentration leads to lower diffusion coefficients. Comparison of the behaviour of NaCl and NaNO<sub>3</sub> is shown in Fig. 5, while that of NaNO<sub>3</sub> as a function of different polymer sulphonation levels is shown in Fig. 6.

#### 4. Results and discussion

The diffusion of ionic species in solution (in water) into a

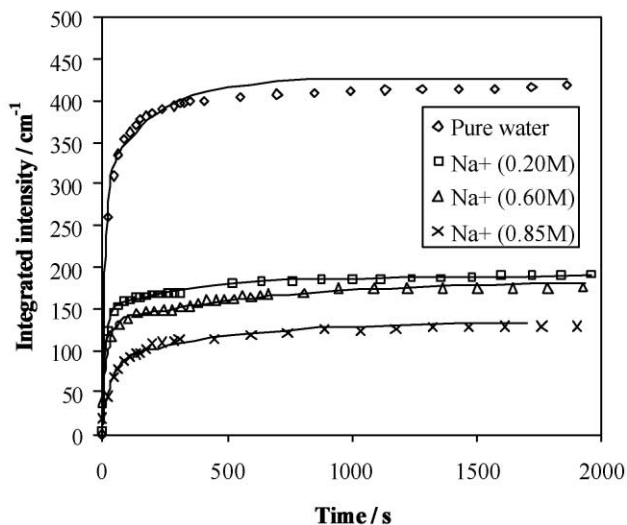


Fig. 4. Comparison of water diffusion curves at different NaCl concentrations.

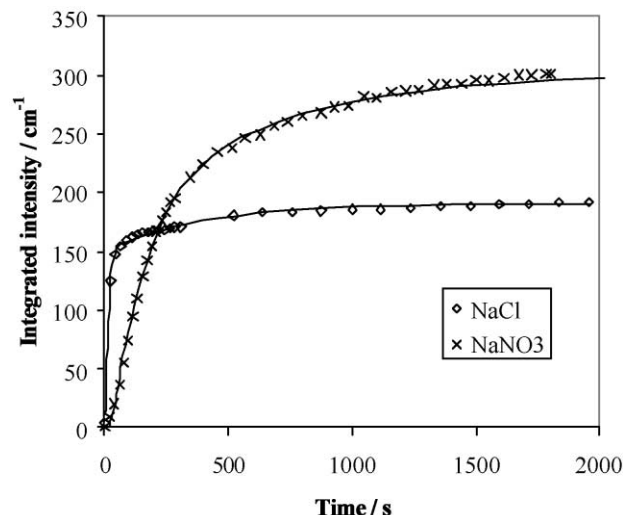


Fig. 5. Comparison of water diffusion curves in NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> containing solutions.

polyelectrolyte film shields the repulsion of the polymer chains (carrying SO<sub>3</sub><sup>-</sup> groups) [1–8]. This should lead to a dramatic reduction in the degree of ‘swelling’ of the polymer (which leads to an increase in the interchain average separation and therefore an increase in volume diffusion rate). Thus, an influx of C<sup>+</sup>A<sup>-</sup> species is expected to lead to a decrease in the water diffusion rate and a corresponding decrease in the water uptake at equilibrium compared with the found in pure water. This is precisely what happens (see Fig. 3 and Table 2). Furthermore, the order of diffusion coefficients of water in the presence of the various cations goes in the order H<sub>2</sub>O > Li<sup>+</sup> > Cs<sup>+</sup> > Na<sup>+</sup> ~ Ca<sup>2+</sup> > K<sup>+</sup>. This is also the order of the water content at equilibrium (Fig. 3) and there is some correlation with the order of the stability of the hydration shells around the various cations (Table 4). However, it would appear that,

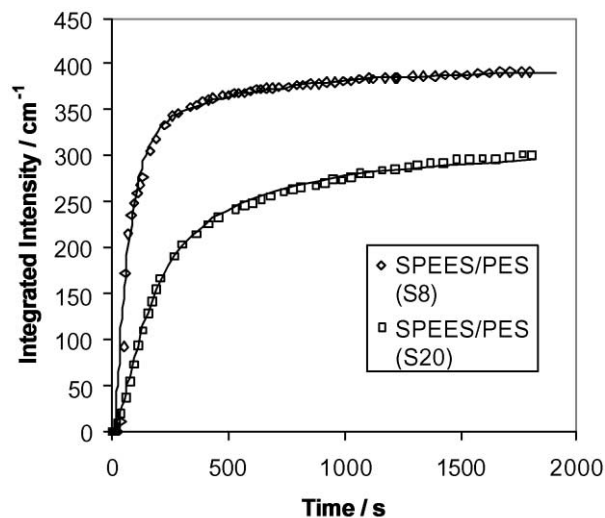


Fig. 6. Comparison of diffusion of water in NaNO<sub>3</sub> solution for S8 and S20 polymers.

Table 3

The dual mode diffusion coefficients and distribution parameter ( $x_1$ ) of water from  $\text{Na}^+$  aqueous solutions with various concentration into SPEES/PES (S8)

Concentration (mol)	$D_1$ ( $\text{cm}^2 \text{s}^{-1}$ )	$D_2$ ( $\text{cm}^2 \text{s}^{-1}$ )	$x_1$
Pure water	$(1.80 \pm 0.3) \times 10^{-8}$	$(5.96 \pm 0.5) \times 10^{-9}$	$0.76 \pm 0.03$
0.2	$(6.76 \pm 0.8) \times 10^{-9}$	$(5.21 \pm 0.5) \times 10^{-10}$	$0.81 \pm 0.04$
0.6	$(4.69 \pm 0.6) \times 10^{-9}$	$(2.66 \pm 0.4) \times 10^{-10}$	$0.71 \pm 0.03$
0.85	$(2.27 \pm 0.4) \times 10^{-9}$	$(1.45 \pm 0.2) \times 10^{-10}$	$0.66 \pm 0.04$

Table 4

Heat of hydration and bare ionic radii of individual ions

Ion	Heat of hydration ( $\text{kcal g ion}^{-1}$ )	Bare ionic radius (nm)
$\text{Li}^+$	-136	0.068
$\text{Na}^+$	-114	0.095
$\text{K}^+$	-94	0.133
$\text{Cs}^+$	-80	0.169
$\text{Mg}^{2+}$	-490	0.061
$\text{Ca}^{2+}$	-410	0.099
$\text{Cl}^-$	-65	0.181

by this token,  $\text{Ca}^{2+}$  ions ought to be more effective at swelling the polymer chains. Water binding to the cation is certainly thought (for example, from the ion transport results reported by Xue et al. [31] on the interdiffusion of hydrogen in couples in Nafion membranes) to be a factor for the degree of polymer swelling in similar systems. Examination of the data for NaCl as a function of concentration (Fig. 4) lends credibility to the swelling scenario. As the concentration is increased from 0.2 to 0.85 M (an increase in the number of ions in solution from 8 to 30 per 1000 water molecules) the diffusion coefficient drops by one order of magnitude, all other experimental variables being the same. This is what is expected if the degree of shielding increases (and the swelling level decreases) with increasing ionic ( $\text{Na}^+$ ) concentration. Even more evidence is provided by a comparison of the data for NaCl and  $\text{NaNO}_3$  (Fig. 5). The larger anion,  $\text{NO}_3^-$ , which is less effective at screening, causes the swelling to be larger and hence the water diffusion coefficient, and the equilibrium water content to be higher for the  $\text{NaNO}_3$  solution.

The use of ATR spectroscopy to monitor water uptake levels and transport coefficients has the additional advantage that the degree of polymer swelling can automatically be monitored by measuring the relative band intensities as a function of time. The swelling process moves the polymeric material (on average) away from the ATR crystal and therefore reduces the band intensities. Fig. 7a shows, for example, the negative going spectral density at particular times along a diffusion experiment (spectra ratioed against the dry polymer spectrum). Fig. 7b shows the integrated spectral data as a function of time for each different cation studies (all at 0.2 M). From this graph—obtained using a 1536–1360  $\text{cm}^{-1}$  integration range it is found that the order of swelling (at equilibrium) is  $\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Cs}^+ \gg$

$\text{Ca}^{2+}$  although the data for  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{K}^+$  are probably the same within the experimental error. So, although sorption of the electrolyte solutions lead to a much lower swelling than for the pure water case (see Fig. 7) the swelling data for the ions does not accord very well with what is expected from the diffusion data (where, for example,  $\text{Li}^+$  solution data should be closest to the pure water data). This is emphasised in Fig. 8. It is, of course, possible that other factors are involved in the interplay of phenomena which control the detailed transport behaviour.

(a) Addition of even modest amounts of salt to water results in a degree of spectral perturbation of the water structure which may affect the relative diffusion

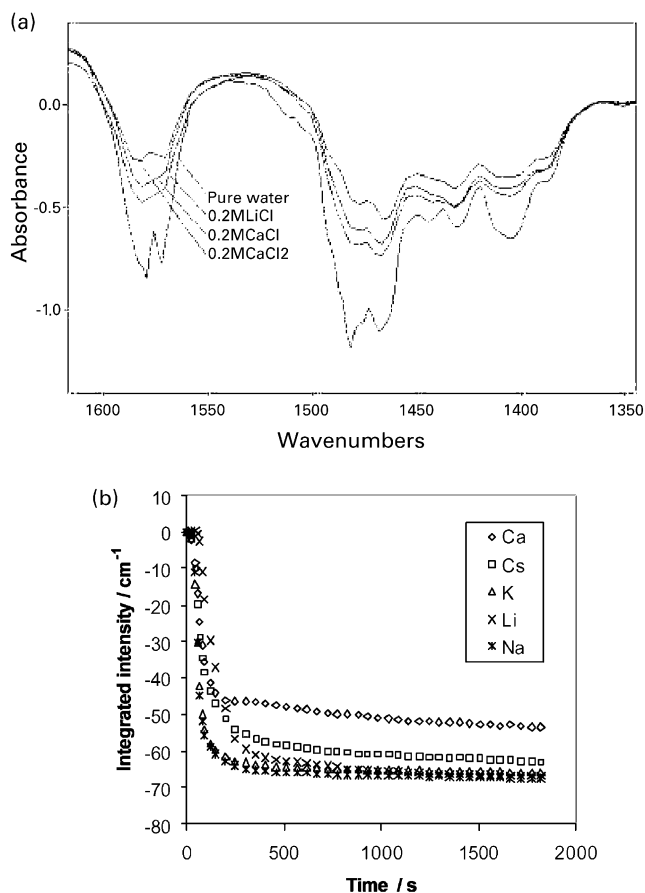


Fig. 7. Diagram showing (a) the different degrees of swelling (from ATR spectra) of SPEES/PES for different electrolyte solutions. (b) A summary of the time dependence of polymer swelling for different cations (all chlorides).

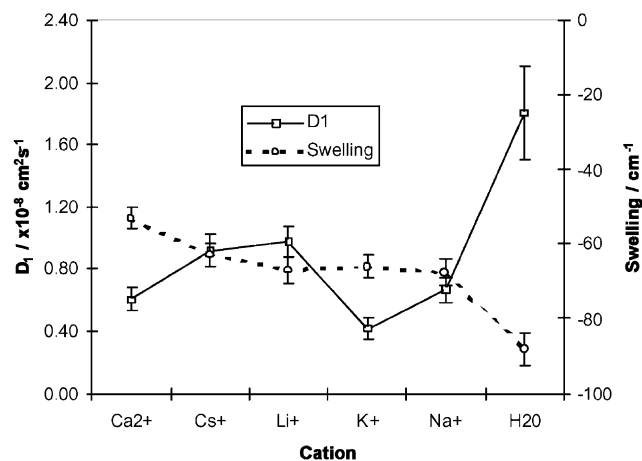


Fig. 8. Summary of the  $D_1$  and swelling data for different electrolyte solutions.

coefficients via differential intensity changes. However, our measurements [32] of the  $\nu(\text{OH})$  band of  $\text{H}_2\text{O}$  in the relevant electrolyte solutions show that such extinction coefficient changes are very small.

(b) In our system, the cations are able to strongly and specifically interact with the anionic  $\text{SO}_3^-$  groups [33–35] (and see Fig. 9) especially if the cation is not too closely bound to water molecules. In fact, the water co-ordination number of most of the cations studied here is  $\sim 6(\pm 1)$  [36–45] (see Table 5) although degrees of  $\text{SO}_3^- \text{C}^+$  ion ‘pairing’ at 0.2 M and the average first solvation shell lifetime, will differ. For example, the  $\text{Ca}^{2++}$  obviously causes a much greater screening of  $\text{SO}_3^-/\text{SO}_3^-$  repulsions by such interactions (the swelling is massively reduced; Fig. 7b) but this does not appear to affect the diffusion rate to the same degree. The transport effects of water/cation  $\text{C}^+(\text{H}_2\text{O})_n$  species with ‘long’ lifetimes is not expected to be significant at 0.2 M since only  $\sim 8$  ions per 1000 water molecules are present in solution (although this ratio is probably higher in the polymer).

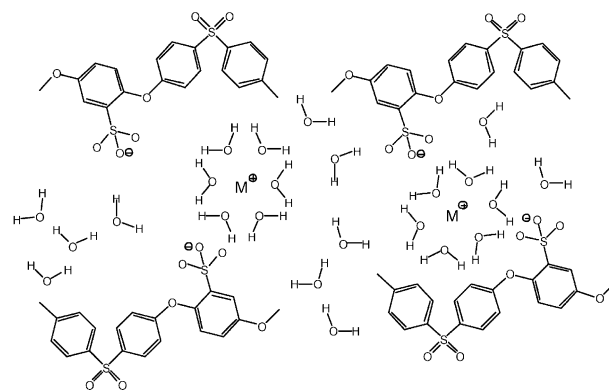


Fig. 9. Possible ion pairing mechanisms at the polymer/liquid interface.

(c) In assessing the relative importance of the swelling using ATR spectroscopy, it is important to bear in mind that the situation may be complicated by changes in extinction coefficients of polymer bands used (in the  $1100\text{--}1500 \text{ cm}^{-1}$  region, see Fig. 7). Such changes, if they were different for different cations, could affect the data shown in Fig. 8 although from previous work on these polymers we regard this as unlikely. Indeed, we believe that the most important uncertainty arises from errors involved in assessing the actual intensity decrease due to swelling. Errors in  $D_1$  (Table 2) might also be a factor (for example for  $\text{K}^+$  solutions). However, the errors are unlikely to cause changes in the order of diffusion rates (Fig. 8).

It is, nevertheless, likely that the data summarised in Fig. 8 are mainly derived from differential degrees of swelling due to different screening levels at the (hydrated) cation–polymer interface. Variations between what is observed and expected purely on this (over-simplified?) basis is likely to be due to complexity introduced by varying factors other than hydration shell stability. It is the detailed nature of the electrical double layer [46] which is important and this may

Table 5  
Co-ordination numbers and ion-solvent distances for aqueous solutions of salts studied

Salt	Concentration (mol)	Cation–oxygen distance ( $\text{\AA}$ )	$r_{\text{c}^+-\text{D}}$ ( $\text{\AA}$ )	Co-ordination number ( $n_{\text{c}^+}$ )	Reference
LiCl	1.0	1.96	2.52	$6.0 \pm 0.5(3)$	[36]
	3.57	1.95	2.55	5.5	[36]
NaCl		2.4		$4.9 \pm 1$	[39,40]
KCl	2.0	3.4–3.8(?)		5.3	[42]
CsCl	2.5–10	3.1		$\sim 7^a$	[39]
	2.8	3.01		5.8 <sup>a</sup>	
MgCl <sub>2</sub>		2.06		5.9	[43]
CaCl <sub>2</sub>	1.0	2.46	3.07	$10 \pm 0.6$	[43]
	1.0	2.42		6 <sup>b</sup>	[39]
	1.1	2.39		6.0	
$\text{Cl}^-$		3.1	2.28	6.4	[41,45]
$\text{NO}_3^-$		2.8	2.8	5	[44,45]

<sup>a</sup> No well-developed solvation shell.

<sup>b</sup> Co-ordination number fixed during fitting to structural model.

depend on the cationic residence time and charge density (i.e. cation–anion interactions) as well as the hydration shell thermodynamics. A non-monotonic variation in diffusion coefficients across (Fig. 8) is, therefore, not entirely unexpected. Further, since the dissociation processes at the  $-\text{SO}_3^- \text{H}$  active sites depend on the level of hydration, the swelling curves of Fig. 7 are expected (as found) to be non-linear.

## 5. Summary and conclusions

We have demonstrated that the major factor affecting the differential diffusion rate of water from electrolyte solutions into SPEES/PES polyelectrolytes is the degree to which repulsion-induced swelling is mediated by  $\text{SO}_3^-/\text{SO}_3^-$  screening by different cations. This effect broadly follows the hydration shell stability of the ions concerned but detailed ‘order’ variations are found in the measured swelling for different cations. This is probably due to variations in the  $-\text{SO}_3\text{H}$  dissociation processes at the ‘double layer’ interface which are highly hydration level dependent.

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