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Sorption and perturbation of water at polyelectrolyte interfaces. Paper 5—effects of water isotopic dilution

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Abstract

We have carefully examined the possible role of local oscillator coupling in D_2O(or H_2O), and locally concentrated evanescent electric fields in creating a large intensity perturbation of the ν(OD) band of water in the polyelectrolytes SPEES/PES (S_5, S_8 and S_{20}). Isotopic dilution experiments lead to the same (or higher) extinction coefficient while an ATR/transmission experimental comparison also gives a similar intensity. We conclude that neither effect is responsible for enhanced P values, and that these must be caused by strong polymer–water interactions at the anionic SO_3^- groups on these polymers.

Keywords: Water diffusion; Polyetherethersulphones; Isotopic dilution

1. Introduction

We have recently reported [1–3] comprehensive studies of the sorption and perturbation of water in sulphonated polyether sulphones (SPEES/PES copolymer) at different levels of sulphonation (and uptake levels of water). We have also explored in some detail [4–7] the reasons for the apparent large deviation from Beer's law which leads to an infrared molar extinction coefficient (for sorbed water ν(OH) band) which is typically one order of magnitude higher than that of pure water (obtained by the same experiment). We have concluded [7] that the most probable origin of such an intensity perturbation is strong water–polymer interactions, which are known to have a significant influence on the water hydrogen-bonding network (and therefore on the ν(OH) vibrational band intensity [8,9]).

However, there are at least two other possible contributions to such an intensity perturbation. One is connected with the possibility of band shape and intensity 'distortion' [10] caused by changes in the intramolecular and intermolecular coupling [11,12] of water molecules in the polymer due to 'clustering' phenomena. The second one is related to the possible heterogeneous distribution of water in the polymer 'voids' or defects, or accumulation of water near the polymer/ATR crystal interface. The first possibility is easily checked by a detailed study of HDO in either H_2O or D_2O (or both). For such solutions the equilibrium concentration of HDO by the reaction [8]

$$H_2O + D_2O \leftrightharpoons 2HDO \qquad K_{eq}^{298} = 3.86 \pm 0.07 \tag{1}$$

can be kept low (typically a few %) with a negligible spectral contribution from D_2O (or from H_2O), for example, for 4% D_2O in H_2O. Thus, it is possible to examine the ν(OH) (or ν(OD)) band (Fig. 1) without the influence of either intermolecular or intramolecular coupling of the OD or OH oscillators. Our initial results [7] seemed to indicate that the relative band intensities were unaltered but a closer look was considered important. Additional information is undoubtedly available from the different band shapes found at different water levels. We attempt to deduce this information in Section 4.2.

The second possibility is examined by a careful ATR vs. transmission spectral study to compare integrated intensities on the same film at the same water (equilibrium) concentration. Accumulation of water at the polymer substrate interface should not affect the average area (or intensity) in transmission mode. However for ATR [13], because the evanescent wave electric field falls off

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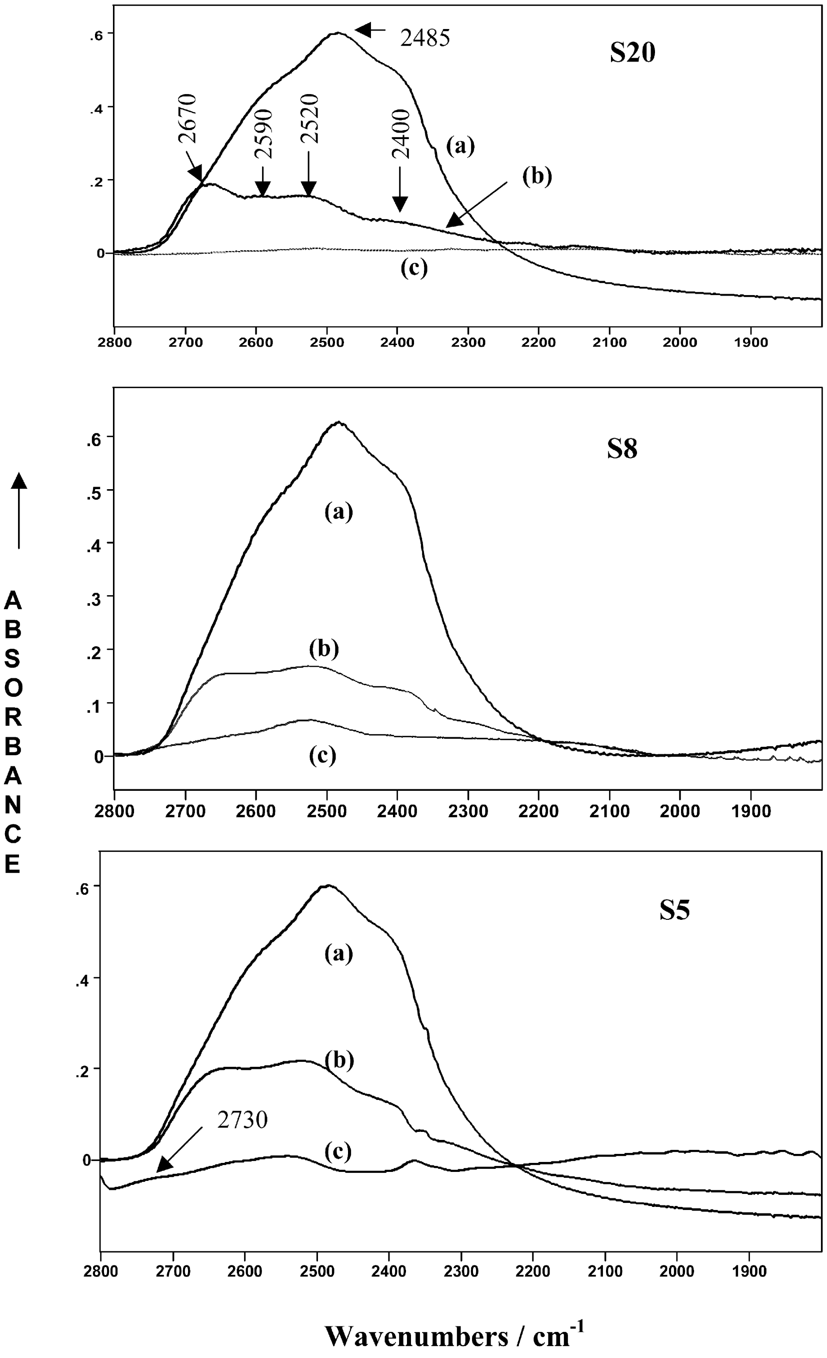


Fig. 1. Band shapes and relative intensities of D_2O and HDO in the SPEES-PES polyelectrolytes S_{20}, S_8 and S_5. (a) D_2O in the pure liquid; (b) 100% D_2O in the polymer; (c) 4% D_2O/96% H_2O in the polymer.

extremely quickly at the crystal/polymer interface, there is a (relatively) very high field near to such an interface.

For example, the IR intensity

$$Int \propto \left(\frac{E}{E_0}\right)^2 \tag{2}$$

and

$$\left(\frac{E}{E_0}\right)^2 = \exp\left(-\frac{2z}{d_p}\right)$$

Where,

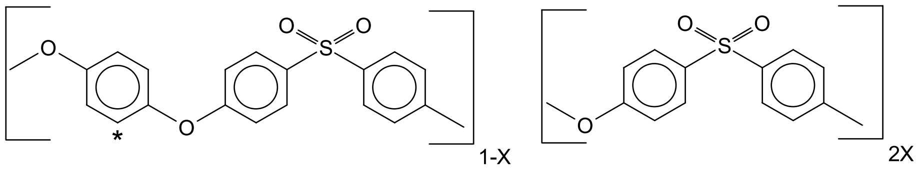
$$d_p = \frac{\frac{\lambda}{n_2}}{2\pi\sqrt{\sin^2\theta - \left(\frac{n_1}{n_2}\right)^2}} \tag{3}$$

Using ZnSe ($n_2 = 2.43$) and a polymer with a refractive index of 1.6 at $\lambda = 3.0$ μm the $(E/E_0)^2$ value has decayed to virtually zero in the first 2.0 μm from the surface. For a 20 μm film, if the majority of water molecules reside (at equilibrium) near the crystal surface, a differential intensity enhancement might be expected (compared with a homogeneous water–polymer distribution). We explore this possibility in Section 4.3

2. Experimental

2.1. Materials

The materials used in this paper were a series of SPEES/PES polymer electrolytes with the following structure



They were obtained from NWW Acumen Ltd (courtesy of Dr Peter Cardew) and were used as received.

The copolymer is sulphonated only at hydroquinone residue * so that the ion exchange capacity of sulphonated polymer is pre-determined by copolymer composition. Sulphonation occurs in 98% H_2SO_4, without degradation.

The degree of sulphonation is characterised by 'S-Number', where

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

Most of the measurements reported here were made on S8 (which has a 12.7% uptake of water).

The ATR crystals used in the experiments were polished 45° silicon (or ZnSe) parallelepipeds (50 mm × 10 mm × 6 mm), purchased 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). FTIR measurements were made by averaging 2 scans on a Mattson Polaris instrument, operating at 4 cm^{-1} resolution, and fitted with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector.

The film-coated crystal was mounted in a flow-through ATR cell (Graseby Specac Ltd) [1–3]. The penetrant (millipore water, 25 °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 dry 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 2 scans; 13 s). The mean value of time was used for determining the diffusion coefficients. H_2O/D_2O mixtures were made up by weight immediately prior to use.

3. Measurements and data treatment

This paper compares the diffusion data and spectral intensities for D_2O and for HDO (Eq. (1)) with those obtained for H_2O previously. This gives a direct measure of any differences, which are caused by inter or intra molecular coupling. The data obtained have been interpreted using the principles elucidated by Fieldsen and Barbari [14], but using the dual mode model [15,16], as we have described before [1–4]. The two diffusion coefficients in this model, although strictly numerical parameters [1,16,19] which arise from the combination of two parallel Fickian diffusion processes, are nevertheless expected to correspond approximately to the (very fast) water sorption at the aqueous/polymer interface and the (subsequent) diffusion of the water into the 'voids' in bulk of the polymer matrix. The water is considered to be partially mobile in both processes [15,16]. 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. (4) and (5).

$$\frac{A_1 - x_1A_0}{x_1(A_\infty - A_0)} = 1 - \frac{8\gamma}{\pi[1-\exp(-2\gamma L)]} \times \sum_{n=0}^{\infty}\left\{\frac{\exp\left(\frac{-D_1(2n+1)^2\pi^2 t}{4L^2}\right)\left[\frac{(2n+1)\pi}{2L}\exp(-2\gamma L)+(-1)^n(2\gamma)\right]}{(2n+1)\left[4\gamma^2+\left(\frac{(2n+1)\pi}{2L}\right)^2\right]}\right\} \quad (4)$$

$$\frac{A_2 - x_2A_0}{x_2(A_\infty - A_0)} = 1 - \frac{8\gamma}{\pi[1-\exp(-2\gamma L)]} \times \sum_{n=0}^{\infty}\left\{\frac{\exp\left(\frac{-D_2(2n+1)^2\pi^2 t}{4L^2}\right)\left[\frac{(2n+1)\pi}{2L}\exp(-2\gamma L)+(-1)^n(2\gamma)\right]}{(2n+1)\left[4\gamma^2+\left(\frac{(2n+1)\pi}{2L}\right)^2\right]}\right\} \quad (5)$$

A is the infrared (ATR) absorbance (at time t), L is the film thickness and γ (Eq. (3)) is the inverse penetration depth in the ATR experiment [13,14]. A_∞ (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 described previously [1,2].

Band shapes and intensities have been measured and treated in the way published previously [1–6]. Band fitting (Fig. 3) was performed using the Grams©32 package with Gaussian/Lorentzian band mixtures.

4. Results and discussion

4.1. Comparison of diffusion coefficients; H_2O and D_2O and water clustering in SPEES/PES polymers

For H_2O it has been demonstrated previously [2] that as the degree of sulphonation decreases ($S_5 \rightarrow S_8 \rightarrow S_{20}$) the diffusion coefficients D_1 and D_2 in the dual mode model Eqs. (4) and (5) decrease monotonically. As part of this study of the effects of isotopic dilution, we have measured the sorption/diffusion coefficients for both D_2O and HDO in a 4%D_2O/96%H_2O mixture. Typical ν(OD) bands are shown in Fig. 1. In Fig. 2, we demonstrate the rather good fit of our data to Eqs. (4) and (5) and we give a summary of the results in Table 1. Again the D_1 and D_2 values decrease with water content and, in fact, are the same (for D_2O) within the experimental error, as the values for H_2O (the small mass effect would not be observable here). The values for HDO do not follow the same obvious trend, but from Fig. 1 it may be seen that the ν(OD) band intensity (2800––1800 cm^{-1}) is extremely low (and may include a contribution from the water (H_2O) combination band [8,9] at ~2100 cm^{-1}). The errors are expected to be much higher. Thus it is not feasible to ascribe D_1 and D_2 differences to the removal of inter or intra molecular coupling. The sorption rates for HDO are of the same order of magnitude as those for H_2O or D_2O as one might normally expect. The zero point energy is not expected to affect transport properties in a 'sorption' sense, although the D_2O/H_2O/HDO differences in vibrational amplitude will affect hydrogen-bond interaction energies [20] at the molecular level (See Section 4.3).

However, transport is expected to be affected by 'clustering' of the water molecules in polymer 'voids' and there is clear evidence for such clustering (see Fig. 1 and our previous papers [4–6]). We therefore consider whether we can assess the degree of 'clustering' using current models.

The Mean Cluster Size (MCS) can be estimated using the interaction parameter χ from the Flory–Huggins equation

$$\ln a = 1 - \Phi_s + \ln \Phi_s + \chi(1 - \Phi_s)^2 \tag{6}$$

thus

$$\chi = \frac{\ln a - 1 + \Phi_s - \ln \Phi_s}{(1 - \Phi_s)^2} \tag{7}$$

The volume fraction of water in the polymer, Φ_s, can be calculated using the amount of water absorbed at equilibrium; as a first approximation, assuming the swelling of the polymer is negligible and $a = 1$ for liquid water.

A MCS, based on the F/H model, was derived by Starkweather [17] as shown in Eq. (8). The results are presented in Table 2.

$$\mathrm{MCS} = \left(\frac{1}{1 - 2\chi\Phi_s} \right) \tag{8}$$

According to Starkweather [17], strong interaction between the water–water molecules at high water content (activity) would increase *MCS* to very high values; implying formation of continuous water domains. For polyelectrolytes—with relatively high equilibrium water levels—this does not seem unreasonable. The Flory–Huggins model (and later, two parameter models; for example, that of Favre et al. [18]) are usually used to interpret the interaction of polymers with water vapour (at variable activity, a). Nevertheless, it is interesting and instructive to look at the *MCS* data produced at $a = 1$ for liquid water in different polymers (Table 2). The values of the interaction parameter increases, and the *MCS* value decreases, as expected, when the number of different sulphonation sites decreases. There is less water sorbed onto the polymer so the interaction per water molecule increases. Conversely, the clustering propensity is expected to decrease because the total water content is lower. Although the absolute values of χ and *MCS* are not expected to be accurate, their relative values are consistent with the heterogeneity changes (via SO_3^- 'defect'

Table 1
Diffusion coefficients for D_2O and H_2O in SPES at 25 °C

Polymer	D_{D2O}		x_1	D_{H2O} Ref. [2]		x_1
	$D_1 \times 10^9$ (cm^2s^{-1})	$D_2 \times 10^{10}$ (cm^2s^{-1})		$D_1 \times 10^9$ (cm^2s^{-1})	$D_2 \times 10^{10}$ (cm^2s^{-1})	
100% D_2O						
S20(5%)	8.3 ± 1.6	8.2	0.8	9.0 ± 1.8	6.5	0.7
S8 (12.7%)	9.7 ± 2.5	13.0	0.8	8.8 ± 2.0	6.2	0.8
S5(20.5%)	10.9 ± 2.0	15.0	0.9	14.0 ± 2.3	14.9	0.9
4% D_2O/96%H_2O						
S20(5%)	8.2 ± 3.1	2.3	0.9			
S8(12.7%)	12.8 ± 2.8	3.6	0.8			
S5(20.5%)	10.9 ± 2.4	–	0.7			

Table 2
Thermodynamic parameters for H_2O–saturated SPEES-PES films

Polymer	Water uptake (w/w)%	Derived interaction parameters		
		Φ_s	χ	*MCS*
S5	20.5	0.26	1.1	2.3
S8	12.7	0.17	1.4	1.8
S20	5	0.07	2.0	1.4

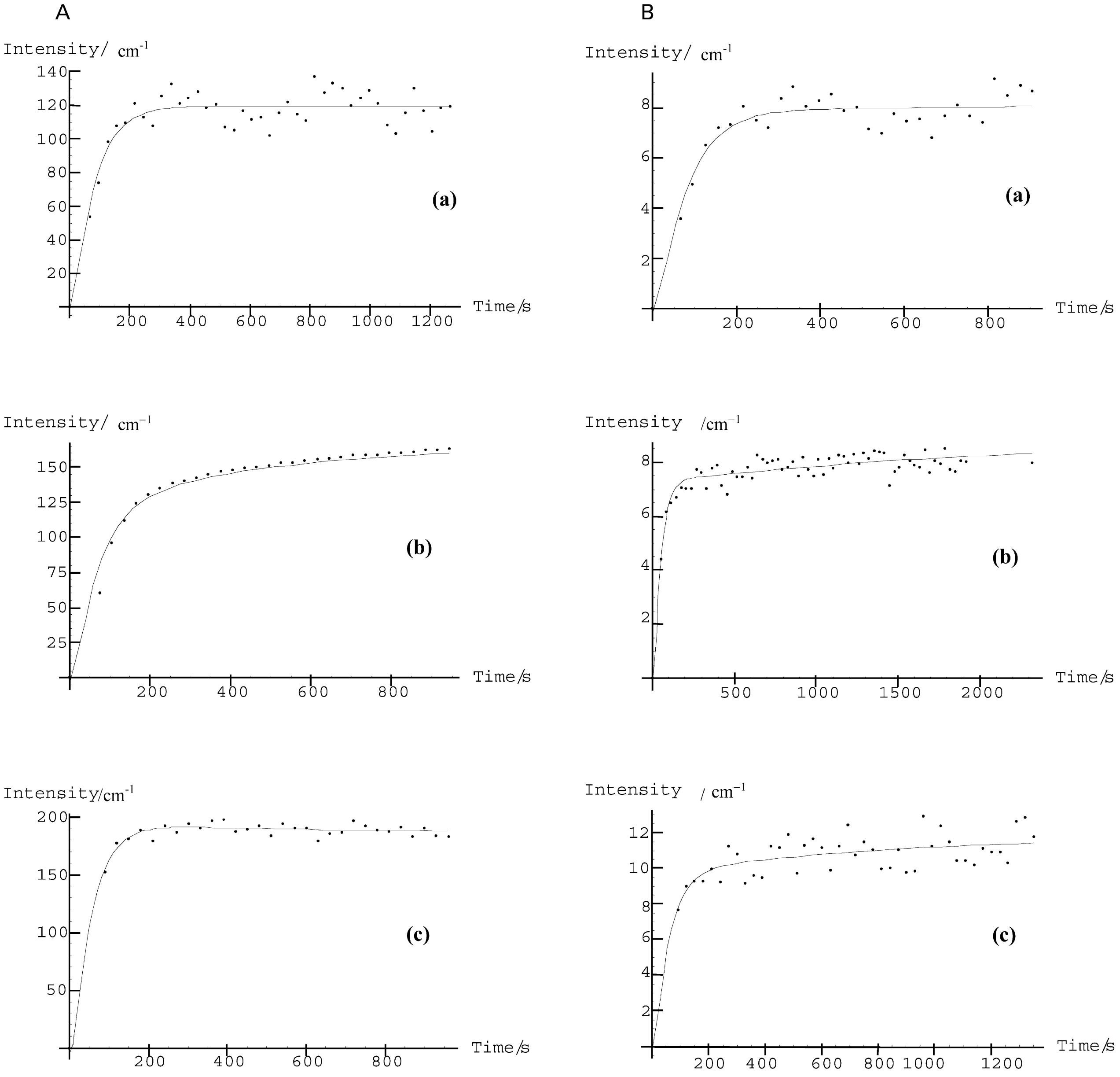


Fig. 2. Diffusion curves for D_2O in the 3 SPEES-PES polymers. In each case the experimental data are compared with best fit to the dual mode model Eqs. ((4) and (5)). (A) 100% D_2O; (B) 4% D_2O in H_2O.

or void distribution) expected for different polymeric functionality.

4.2. Elucidation of band shapes and intensities for H_2O, D_2O and HDO

Figs. 1 and 3 demonstrate a number of interesting features of the ν(OD) band shape at 100% and 4% D_2O in the polymer (compared with the spectrum of the pure liquid). Because the coupled oscillator ν(OD) width is considerably lower for D_2O than for H_2O it is considerably easier to establish that the band profile has sub-maxima (as was assumed in Ref. [5]) attributable to different water environments (in the mixture model [10,11,19]). For S_5 and S_8 polymers there seem to be 3 principal band components near 2650, 2520 and 2390 cm^{-1} (Table 3). There may be other smaller bands associated with a very long spectral tail between 1900 and 2300 cm^{-1}, the origin of which is not clear. These data compare with principal band positions [8] of 2685, 2590, 2480 and 2380 cm^{-1} (in the pure liquid). Three of the ν(OD) band positions 'match' very well between D_2O in the polymer and in the liquid. The relative intensities of the bands at highest frequencies (i.e. lowest average hydrogen bond strengths) are, however, larger in the polymer as found many times for water in polymers. This indicates that the water network is broken in the polymers 'voids' giving, on average, smaller cluster sizes.

For the HDO, ν(OD), bands in the polymer (Fig. 3B)

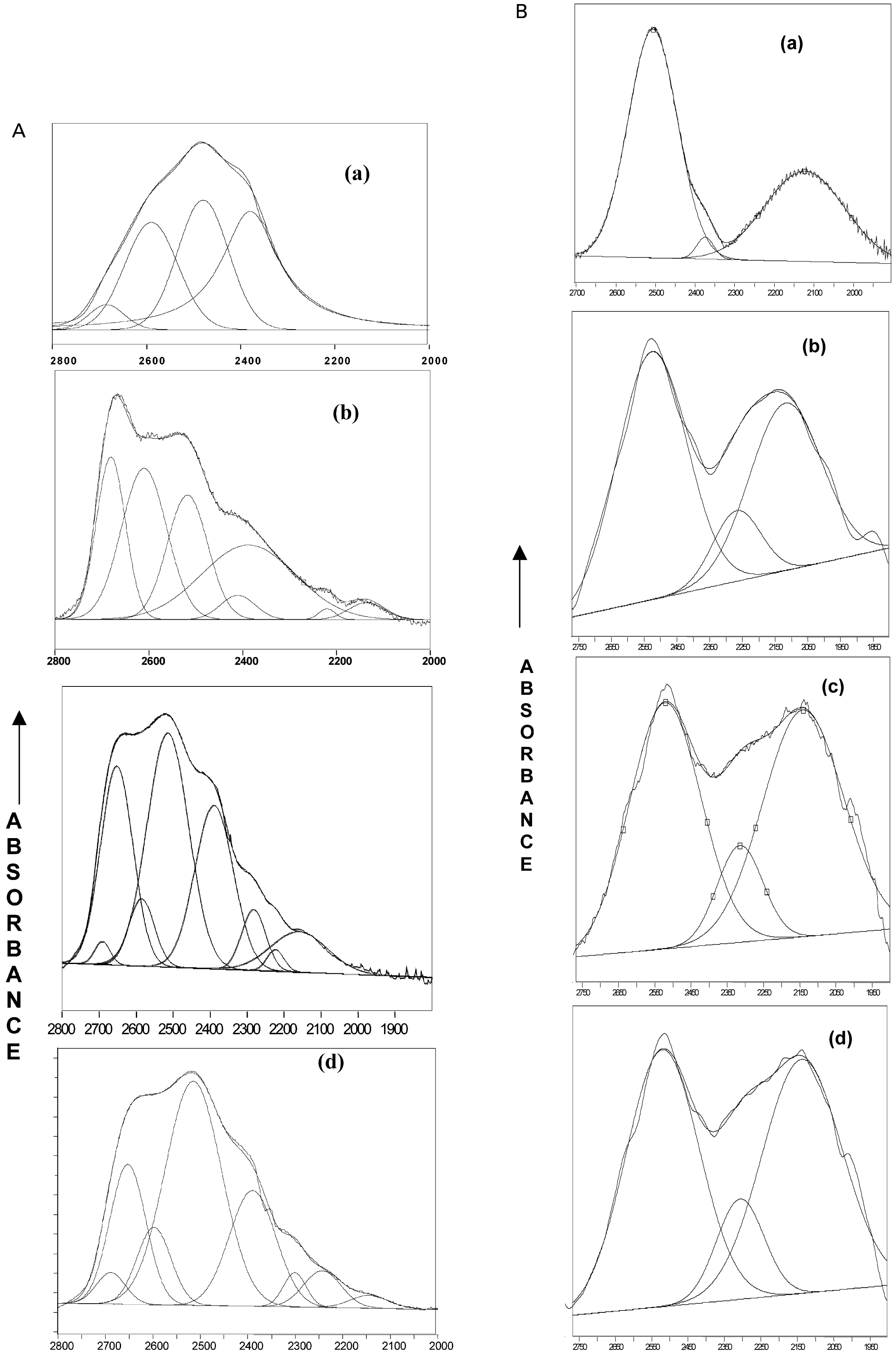

A
(a)
2800 2600 2400 2200 2000
(b)
2800 2600 2400 2200 2000
ABSORBANCE
2800 2700 2600 2500 2400 2300 2200 2100 2000 1900
(d)
2800 2700 2600 2500 2400 2300 2200 2100 2000
Wavenumber / cm-1
B
(a)
2700 2600 2500 2400 2300 2200 2100 2000
(b)
2750 2650 2550 2450 2350 2250 2150 2050 1950 1850
ABSORBANCE
(c)
2750 2650 2550 2450 2350 2250 2150 2050 1950
(d)
2750 2650 2550 2450 2350 2250 2150 2050 1950
Wavenumber / cm-1

Table 3
Curve-fitting results for D_2O in S20, S8 and S5

System	Centre/cm^{-1}	FWHM/cm^{-1}	Area (%)
100%D_2O on blank Si	2685	88.5	4.1
	2590	133.0	25.7
	2480	127.7	29.8
	2380	145.9	40.4
S20	2681	72.9	63.6
	2610	113.5	19.6
	2518	101.9	14.7
	2410	86.4	2.1
S8	2653	105.2	29.3
	2587	78.4	6.1
	2515	134.6	38.4
	2390	122.1	26.3
S5	2653	97.9	25.0
	2598	83.9	7.8
	2515	139.9	41.1
	2390	125.2	26.1

there is only one principal band near 2550 cm^{-1} (with a shoulder to higher frequency -2650 cm^{-1} and a smaller feature near 2350 cm^{-1} (as found in the liquid). This pattern is similar to that found in 'liquid' HDO [8] where the bands are at 2670, 2525, 2475, and 2400 cm^{-1}. The main band is accompanied by the combination band of H_2O at ~2150 cm^{-1} $(\nu_b + \nu_L)$. The 2650 cm^{-1} shoulder, produced by weaker hydrogen bonded clusters is particularly evident (Fig. 4) in the case of 4% D_2O in S_{20} where we have a lower SO_3^- concentration, weaker water–water interactions (see Section 4.1) and smaller water clusters. This ties in nicely with a lower calculated 'mean cluster size' at lower SO_3^- levels (Table 2). Thus, the ν(OD) band structure appears simpler for HDO compared with D_2O (as expected for decoupled OH and OD oscillators) but the overall behaviour in the liquid and in the polymer is broadly the same as that for D_2O (or H_2O [1–4]).

The question of whether the apparent water intensity perturbation is somehow connected with inter- or intra-molecular coupling of H_2O or D_2O has been addressed by detailed examination of the P factors [4–6] obtained in the polymer for D_2O and HDO (values given in Table 4). The P value is a weighted extinction coefficient ratio for 'water' in the polymer, compared with pure water. Following [5], this enhancement factor $P$is calculated using Eq. (9).

$$P = \left(\frac{C_w}{C_p}\right)\left(\frac{d_w}{d_p}\right)\left(\frac{Area_p}{Area_w}\right) \tag{9}$$

to give a direct measure of the electronic perturbation of water molecules trapped in polymer 'voids. As Table 4 shows, the values of P are higher for the HDO molecule than they are for D_2O. They are certainly not any lower due to local oscillator decoupling. Indeed, they are closer to the values found for H_2O [4–6]. There seems no logical reason why the ν(OD) oscillator should be affected more (or less) by the 'chemically' based intermolecular forces between polymer and water [6]. The same order of magnitude of perturbation is expected (as found). We conclude that oscillator coupling is not responsible for the enhanced P values. Indeed, it may lead to a suppression of the effect, although it is not easy to see why this should be the case.

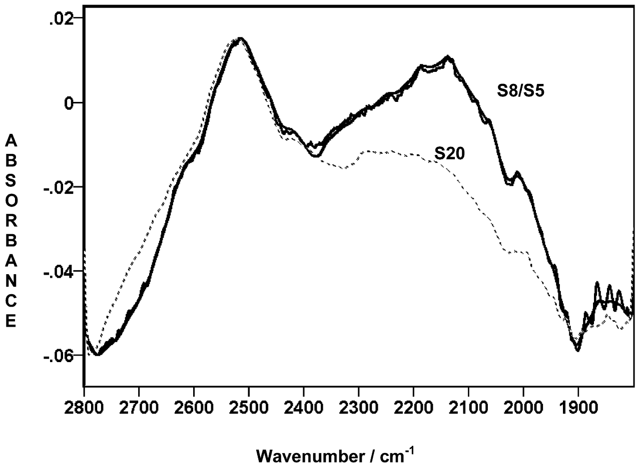


Fig. 4. A detailed assessment of the ν(OD) bandshape of HOD at 4% D_2O/96% H_2O in the polymers, S5, S8 and S20.

We conclude that, although the 'decoupled' ν(OD) band of HDO is simpler, as expected, than for the 'coupled' ν(OD) band of D_2O, there is little evidence that the observed intensity perturbation for water 'clusters' in the polymer matrix is significantly affected.

4.3. Dependence of band intensities and band shapes on method of measurement

As discussed in the introduction the only way of assessing whether or not the perturbation P is caused by heterogeneity of water 'phase' distribution in the polymer (and hence selectively enhanced evanescent fields) is to compare the band intensities for the saturated polymer in ATR and in transmission. This is not easy for reasons outlined in Ref. [6]. Essentially, it is difficult to adjust the polymer film thickness and experimental conditions in such a way that a reasonably intense, but non-saturating, band profile can be measured by the two techniques for the same material. Nevertheless, this is a very important experiment to check out because a non-uniform distribution of the water molecules near the ATR crystal/ polymer interface would

Fig. 3. Gaussian/Lorentzian ν(OD) band fits for 100% and 4% D_2O in the liquid and in SPEES-PES polymeric films. Only the 4 principal bands have been interpreted in each case—see text); 3A (a) 100% D_2O; (b) 100% D_2O in S_{20}; (c) 100% D_2O in S_8; (d) 100% D_2O in S_6; 3B (a) 4% D_2O/96% H_2O; (b) 4% D_2O/96% H_2O in S_{20}; (c) 4% D_2O/96% H_2O $_{in}$ S_8; (d) 4% D_2O/96% H_2O in S_5.

Table 4
Intensity and enhancement factor P of ν(OD) in various environments

System	Integrated band intensity (cm^{-1})			P factor		
	S_{20}	S_8	S_5	S_{20}	S_8	S_5
100% D_2O in SPES	55	68	80	2.0	2.6	3.0
4% D_2O in SPEES/PES	4.1	4.7	4.7	9.7	4.9	3.8

lead to a severe intensity perturbation. A rough estimate of this effect can be obtained by integrating Eq. (3) over the region near the interface. The ratio of IR intensities for a given oscillator transition dipole is given by

$$\text{Ratio} \propto \frac{\int_0^{2\mu m} \exp\left(-\frac{2z}{d_p}\right)dz}{\int_{2\mu m}^{20\mu m} \exp\left(-\frac{2z}{d_p}\right)dz} \approx 200 \tag{10}$$

where the figures are appropriate to ZnSe at $\lambda = 2.8$ μm with $d_p = 0.7$ μm. Thus if all the water molecules were concentrated near (but not at) the interface, a factor of 10 in the 'intensity' (i.e. measurement extinction coefficient) could easily be generated (compared with the pure liquid, where the molecular distribution is uniform). Although the molarity of water in the polymer (S_8) is approximately 6.6 M (mf = 0.66), and the number of water molecules per polymer repeat unit is 66/100, an extremely non-uniform distribution would lead to a severely enhanced P value. In other words, the effective C_p used in Eq. (9) would be incorrect.

Fig. 5 shows our best efforts to do this experiment. The band shapes of the two profiles are different. It is well known [21,22] that ATR band shapes are affected by changes in refractive index through the band. However, it is clear that the overall band areas for a given system are very similar. We need to remember that the two experiments sample the material in different ways. The transmission experiment samples the whole film once. The ATR experiment samples the film ~10 times, but only samples the first 2 μm near the interface. For a film of 20 μm thickness (assuming the same perturbation of intensity) the two intensities should be identical. Our 'transmission' film was ~5 μm in thickness so the ATR intensity should be higher than the transmission intensity. However, two intensities are clearly the same order of magnitude and this leads us to conclude that the local concentration of evanescent field at the polymer/crystal interface is not responsible for an enhanced P value. This also adds weight to our previously published analysis [6,7] which speculates that the water–polymer interactions are responsible for the high P values.

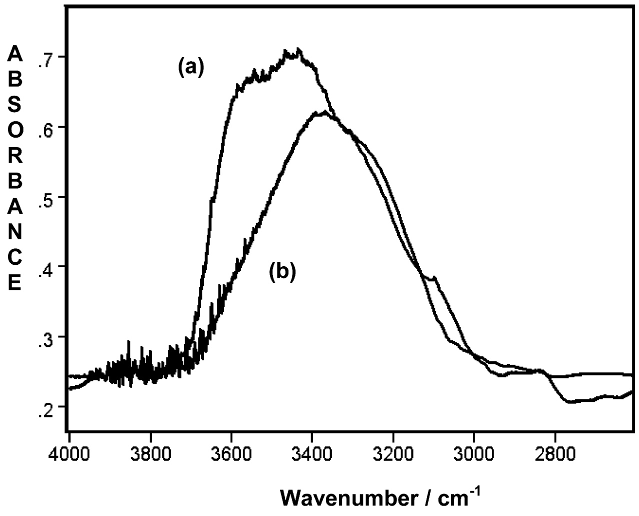


Fig. 5. Comparison of transmission (a) and ATR spectra (b) of SPEES-PES S_8 saturated with a 4% D_2O/96% H_2O mixture.

5. Summary and conclusions

The infrared intensity perturbation found for water sorbed onto SPEES-PES polyelectrolytes has been explored as a function of isotopic dilution and as a function of the FTIR sampling method. The use of ν(OD) band of HDO (4% D_2O in 96% H_2O)—leading to both intramolecular and intermolecular de-coupling—gave similar order perturbation (P) values, demonstrating the lack of dependence of extinction coefficient on such coupling. The comparison of ATR and transmission experiment also led to similar band intensities. This confirms that there is no microscopic concentration gradient towards the polymer/substrate interfaces (in accordance with the work of Vesely [23]). We are driven to the conclusion reached previously [4–7] that the high intensity perturbation is due to strong water–polymer interactions arising from a microscopically heterogeneous distribution in the polymer 'voids' or 'defects'.

Acknowledgements

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References

[1] Pereira MR, Yarwood J. J Chem Soc-Faraday Trans 1996;92:2731–5. Pereira MR, Yarwood J. J Chem Soc-Faraday Trans 1996;92: 2737–43.
[2] Hajatdoost S, Yarwood J. J Chem Soc-Faraday Trans 1997;93: 1613–20.
[3] Hajatdoost S, Yarwood J, Sammon C. Polymer 2002;43:1821–7.
[4] Yarwood J, Sammon C, Mura C, Pereira M. J Mol Liq 1999;80: 93–115. Yarwood J, Sammon C, Mura C, Pereira M. J Mol Liq 2002; 96/97:305.
[5] Sammon C, Mura C, Yarwood J, Evarall N, Swart R, Hodge D. J Phys Chem 1998;B102:3402–11.

[6] Deng C-S, Sammon C, Yarwood J. Polymer 2003; in press.
[7] Deng C-S, Sammon C, Mura C, Yarwood J. J Mol Liq 2002;101: 30–54.
[8] Libnau FA, Christy AA, Kvalheim OM. Appl Spectrosc 1995;49: 1431–7.
[9] Marechal Y. J Chem Phys 1991;95:5565–73. Marechal Y. J Phys (France) 1993;3:557–71. Marechal Y. J Mol Struct 1994;322: 105–11.
[10] Falk M. Can J Chem 1980;58:1495. Falk M. Chem Phys Aqueous Gas Solutions Electrochem Soc Princeton 1975;19–41.
[11] Hare DE, Sorenson CM. J Chem Phys 1992;96:13–22. Hare DE, Sorenson CM. J Chem Phys 1990;93:6954–61.
[12] Luck WAP. J Mol Struct 1998;448:131–42.
[13] Mirabella F. Appl Spect Rev 1985;21:45.
[14] Fieldson GT, Barbari TA. Polymer 1993;34:1146.
[15] Veith WR, Howell JM, Hseih JH. J Membr Sci 1976;(1):177.
[16] Veith WR. Diffusion in and though polymers, principles and application. New York: OUP; 1991.
[17] Starkweather HW. J Polym Sci 1963;1:139.
[18] Favre E, Clement R, Nguyen QT, Schaetzel P, Neel J. Chem Soc Faraday Trans 1993;89:4347.
[19] Walrafen GE, Fischer MR, Hakmatadi MS, Yang WH. J Chem Phys 1986;85:6964. Walrafen GE, Fischer MR, Hakmatadi MS, Yang WH. J Phys Chem 1983;92:2433.
[20] Hallam HE. In: Davies MM, editor. IR Spectroscopy and Molecular Structure. Amsterdam: Elsevier; 1963. Lowry TH, Richardson KS. Mechanism and Theory in Organic Chemistry. New York: Harper and Raw; 1981.
[21] Hancer M, Sperline RP, Miller JD. Appl Spectrosc 2000;54:138.
[22] Max J-J, Chapados C. Appl Spectrosc 1999;53:1045.
[23] Vesely D. J Polym Sci Polym Phys 1986;24:1869.