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Polymer–water interactions. Origin of perturbed infrared intensities of water in polymeric systems

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Abstract

We explore the possible reasons for the huge infrared intensity perturbations of water molecules sorbed onto a variety of polymer surfaces. We demonstrate that strong polymer–water interactions, not always obvious from qualitative approaches to examination of the water vibrational spectra, are probably responsible for such effects. The deviations from Beer's law for water adsorption is semi-quantitatively correlated with the level of water uptake (i.e. water activity in the polymer). This clearly demonstrates the dependence on water–polymer proximity and intermolecular interaction strength, to the extent that donor–acceptor charge transfer interactions may well control this interesting, and potentially useful, phenomenon.

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Keywords: Polymer; Water; Infrared intensities; Molecular interactions

1. Background and Introduction

Several years ago [1,2] we showed that water sorbed onto either PET [1,2] or PVC [1,3] thin films gave FTIR ATR spectra showing distinct and very substantial deviations from Beer's law (Fig. 1). The perturbation parameter P (see Section 4) has values [1–3] of between 10 and 50 depending on the spectral region of the ν(OH) band profile examined. As far as we are aware, the origin of this effect has not been discussed in the literature. However, there have been some notable cases of confusion which have arisen [4,5] because changes in extinction coefficient, as a function of water 'sorption', have not been considered. There are probably many more such cases.

It is, of course, not unreasonable to expect an infrared intensity increase, since the IR transition dipole is known [6–10] to be extremely sensitive to molecular 'environment' and to electronic perturbations. Indeed, gas → liquid phase transitions routinely result [6,7] in an intensity increase, for many of the vibrational modes, by an order of magnitude; sometimes higher.

Such electronic perturbation results from intermolecular forces which are operative in all condensed phases, but whose nature and strength may change depending on the local chemistry, proximity, etc. It is fully expected, and clearly established in liquids, that intermolecular forces effect the molecular dynamics [11–14] including rotation diffusion coefficients [13,14]. These are reflected in measured mean squared torques [11–14].

Hydrogen-bonded 'interactions' are usually considered to be dominated by electrostatic forces, at least as far as the interaction energy is concerned [6,15–17]. These are of course, the most obvious example of such electrical perturbations, and much literature [6,7,16–18] has been generated describing intensity increases of both proton donor and proton acceptor molecular spectra on this basis. Our current paper examines the evidence that the large observed water intensity increases are, in fact, due to the changes in intermolecular forces, when the molecules are sorbed by a polymer, and explores whether or not those forces are likely to be electrostatic in nature.

2. Review of previous work

Experimental evidence that water–polymer interactions are important origins of the behaviour of such systems has been collected for many years. This is particular true for

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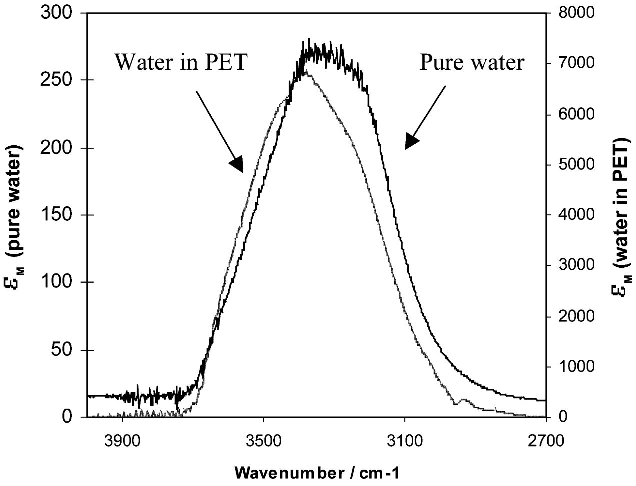


Fig. 1. Comparison of the FTIR/ATR ν(OH) band intensities of bulk water and 1% water in PET at 25 °C.

water at biological polymer (i.e. protein) interfaces [19,20], in organic coatings [21] and in food based materials [22,23] (such as starch and cellulose). However, as recently pointed out by Vesely [24], the detailed origin of such interaction forces is considered rather speculative. Nevertheless, there have been simplified calculations of model 'functional' group–water interactions [25–27] which show that the classical Gibbs free energy of interaction is likely to be of the order of $-25\ \mathrm{kJ\ mol^{-1}}$ for 'hydrophilic' groups (e.g. OH, C=O, etc.) and $+1$–$2\ \mathrm{kJ\ mol^{-1}}$ for 'hydrophobic' groups (e.g. $-\mathrm{CH_3}$). Such interaction 'strengths' seem to be 'universal' (and therefore maybe subject to large 'cancellation of errors' effects?). So, they give little feeling for the different interaction levels expected; for example, at different hydrophilic surfaces (on different polymeric sites).

Distinctive and definitive evidence for polymer–water interactions obtained using vibrational spectroscopy is not easy to find. 'Finger-printing' ought to provide unequivocal 'markers.' However, because the fundamental band formation processes (for water) lead to either very high (absorption) or very low (scattering) cross sections, one needs to deal with either very low or very high (respectively) 'concentrations' and hence with special sampling techniques [1–3,28–32]. The level of interpretation is, even then, considered to be ambiguous (see discussion in Ref. [19] pp. 379–389). Nevertheless, there have been many attempts to record such markers and use them to elucidate the interactions which lead to the observed electronic perturbation. Refs. [1–5,33–47] give a selection of the recent work in this area using IR [5,27–29,33–39, 40–42] and Raman [28,32,43,44,47] spectroscopy, where polymer–water interactions have been especially considered. Relatively few papers have, however, examined the infrared [1–3,33,34,41,42] or Raman [28,43,44,47] intensities in detail. Furthermore, as far as we are aware there has been only one recent paper [5] which alludes to the possible effect of charge transfer [7,15,17] on the water ν(OH) band intensity profile in a polymeric system. There are, however, reports of such intensity increases in microcrystalline ice [48] and in electrolyte solutions [49].

There is a considerable body of literature [51–58] (driven mainly be membrane separation science) associated with the characterisation of cellulose acetate (and related) asymmetric membranes manufactured by phase inversion [53]. This technique allows some control of surface morphology, and in particular, the pore size and distribution. For these materials, a good correlation has been found between the FTIR-ATR ν(OH) band shape and the pore size/surface morphology of the polymer [53–55]. There are significant effects on the overall shape of the band (Fig. 1 of Ref. [53]) as one goes, for example, from a 6 to an 80 Å pore size system [58]. These have been interpreted in terms of the ability of water of hydration to form 'clusters' of different sizes and interaction strengths. For the polymers considered here, there are undoubtedly a range of water molecule environments (both for a given polymer and between different chemical and/or physical situations). However, it is difficult to correlate such data with pore size (which we do not know). On the other hand, the infrared intensity gives a rather convenient handle on the polymer–water interactions through the proximity of water (at different levels) to the hydrophilic 'pore' surface.

3. Experimental

The polymer films used to generate the data given in this paper were produced by solvent evaporation in the way described in our previous papers [50]. They are all dense films without (as far as we are aware) any active layer 'asymmetry'. We do not have a direct measure of the pore distribution or size since we have measured only water sorption (rather than permeability) rates. We have, however, made AFM measurements of surface roughness. The value obtained, for example, for the $\mathrm{S_8}$ polyelectrolyte (SPEES/PES) (which appears to retain a similar water content as cellulose acetate) was RA = 5.1 Å. This seems very smooth compared with those obtained by phase inversion. FTIR-ATR band structure for this polymer [50] at equilibrium saturation shows a very similar shape to that reported by dePinho and co-workers [53] for an asymmetric or dense film of cellulose acetate. It seems likely therefore that the average pore or void sizes are similar (of the order of 100 Å), although the CA distribution might be quite different. Although the water 'clustering' (in both cases) is 'weak' relative to 'bulk' water, the band shape in the polymer indicates that the water–water interactions are not dissimilar to those in bulk water. However, the intensity of the ν(OH) band clearly indicates the strong water–polymer interactions, regardless of pore size.

4. Results and discussion

We have examined the perturbation *P* factor [1–3,50] for a series of polymers (polyethylene terephthalate (PET), polyvinyl chloride (PVC) and polyether sulphones, SPEES/PES) containing (at equilibrium) different amounts of water; from ~1 to ~20% (by weight).

$\underline{P}$ is defined, very simply by,

$$\underline{P} = \left(\frac{C_\mathrm{w}}{C_\mathrm{p}}\right)\left(\frac{d_\mathrm{w}}{d_\mathrm{p}}\right)\left(\frac{\mathrm{Area}_\mathrm{p}}{\mathrm{Area}_\mathrm{w}}\right) \qquad (1)$$

(where C_i, d_i and Area_i refer to concentration, ATR-depth and band area for pure water or sorbed water).

$\underline{P}$ is a measure of the overall deviation from Beers law represented by data such as those shown in Fig. 1. The values are summarised in Table 1 and plotted as a function of sorbed water content in Fig. 2. This, now reasonably well-established, phenomenon was initially considered to be counter intuitive since the shift to *higher* frequency, at the same time as an intensity *increase* was seen to be contradictory. It is well-known [6,7,17,18] that an *increase* in HB strength leads to an IR intensity increase, while the observed shift to high frequency is representative of a loosening of the hydrogen bonding (of the water–water interaction!) (as is found by other techniques [29–31]).

We therefore need to explore the full range of possible influences in our system which may affect the intensity perturbation of the ν(OH) band of water molecules (sorbed onto a polymer).

(i) That the intensity change is due to water 'network' breaking.

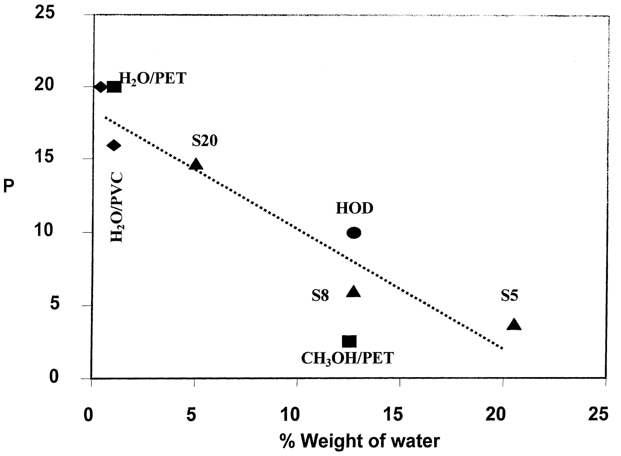


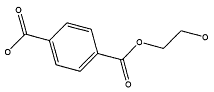
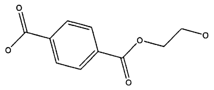
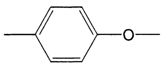
Fig. 2. Correlation of intensity factor *P* with up take of water in a range of polymers (S_5, S_8 and S_{20} are SPEES/PES polyelectrolytes with varying exchange capacities, see Ref. [50]).

(ii) That the ATR 'evanescent' field is a selectively perturbing influence.
(iii) That intermolecular or intramolecular coupling of the water molecules affect the bandshape (and hence the intensity behaviour).
(iv) That 'percolation' effects in the polymer lead to an intensity increase.
(v) That water–polymer interactions are sufficient to cause such a large intensity increase.

4.1. The effects of network breaking

Water behaves as a tetrahedral network (albeit with a short lifetime) in the pure liquid and there is good evidence that small clusters of water molecules are formed in a

Table 1
Summary of *P* values for H_2O in polymers studied

Polymer	Solute	% Solute at equilibrium	$\underline{P}$[a]	Chemical groups	IP (eV)
PET	H_2O	1	20 ± 0.5		8.9(C=O)
	CH_3OH	12.5	2.5		
PVC	H_2O	1	16 ± 0.5	Cl, $-CH_2-CH-$	11(Cl)
PVC/DOP[b]	H_2O	0.35	~20	 Cl, $-CH_2-CH-$	
SPEES/PES, S8	H_2O	12.7	6.2 ± 1.5	, $S0_2$, $S0_3^-$, H_30^+	~8(SO_n^-)
	HOD[c]	12.7	10–13		
	D_2O	12.7	~6		

[a] ν(OH) band of coupled oscillators unless otherwise stated.
[b] Plasticised material.
[c] ν(OD) band HOD (4% D_2O in H_2O).

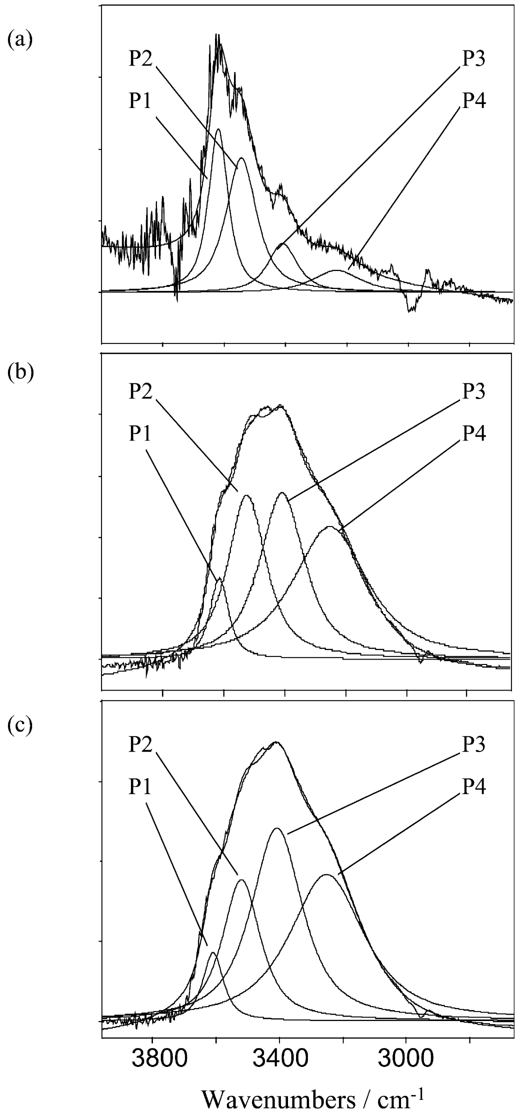


Fig. 3. Demonstration of evolving FTIR/ATR ν(OH) band shapes for water in PET as a function of time after (a) 1, (b) 10, and (c) 30 min.

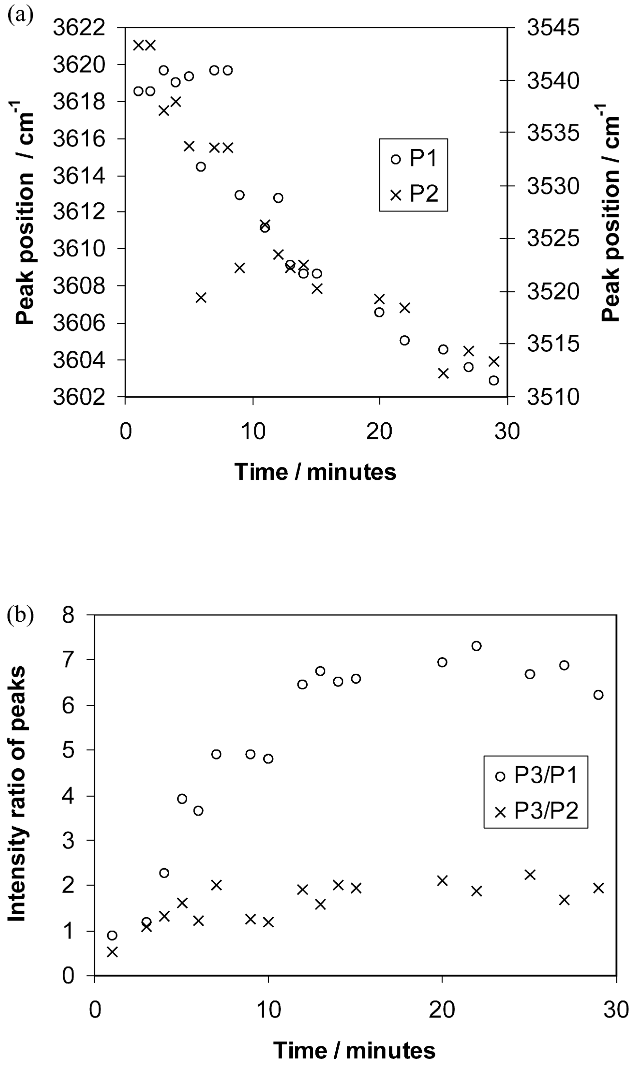


Fig. 4. Frequency shifts (a) and intensity ratios (b) of the P1–P3 components (shown in Fig. 3a–c) if the ν(OH) band of water in PET over a 1–30 min time period.

polymer at low concentrations. The data shown in Fig. 3 have been obtained at short times for the sorption of water into PET. The band profile can be decomposed into four bands (as found previously [2]). At the shortest times-up (to about 5 min) the weakest hydrogen bonded species have the largest relative intensities and highest frequencies (as illustrated in Fig. 4a). It has been nicely demonstrated [59] that the ν_1 band of water is usually not observed at low water 'densities' (because of low extinction coefficient). We therefore expect the bands at 3620 and 3545 cm^{-1} to be due to small weakly hydrogen bonded water clusters. Indeed, the presence of small cyclic clusters; dimers, trimers, etc. has been inferred in the low density IR spectra of pre-critical water [60]. However, in a polymeric system the exact nature of the water aggregates is more difficult to surmise. Larger clusters (3410 and 3235 cm^{-1}) are present in relatively small amounts. As the water concentration increases, both water–water and water–polymer interactions increase and both the relative intensity decrease and shifts to low frequency of the P1 + P2 bands show monotonic changes in time (Fig. 4) Since the formation of small clusters amounts to a reduction of symmetry ($T_d \rightarrow C_{2v}$, in the monomer limit) one might consider the additional intensity caused by addition 'modes' However, it is well-known (Ref. [6] p. 35) that the liquid water/water vapour band intensity ratio is 12 and it is unlikely that small cluster formation can lead to an increase in intensity.

4.2. The effect of evanescent wave, electric field

There is some evidence that very thin films may suffer an 'effective thickness' enhancement (the equivalent of an intensity increase) as a result of confinement in the electric field close to the ATR crystal. The results of this effect,

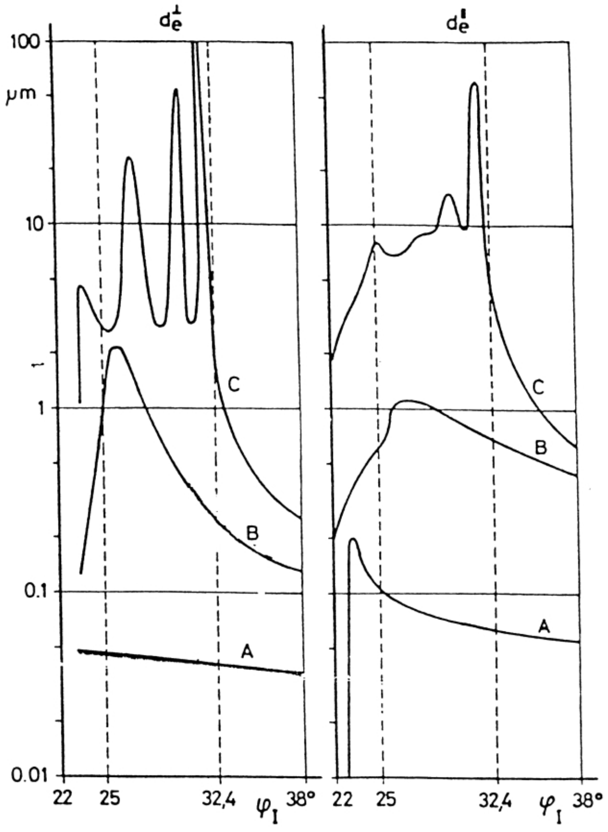


Fig. 5. Effective thickness (i.e. intensity enhancements) in the ATR evanescent field as a function of incidence angle, for an argon matrix on KRS5 ($n = 2.37$, $\lambda = 1$ µm $K = 10^{-4}$. (A) $d = 0.02$ µm; (B) $d = 0.2$ µm; (C) $d = 2.0$ µm (reproduced by permission, from Ref. [61]).

calculated by Hüber-Walchli and Günthard [61], are given in Fig. 5. Since, for ATR optics

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

and IR intensity is proportional to

$$[E/E_0]^2 \tag{3}$$

the electric field at the near surface (from which the ATR IR spectra of sorbed water molecules emanate) is relatively high.

For thin films, $\ell < d_p$ (d_p is the depth of penetration) enhancement shows that factors of 3–50 may be obtained. The 'oscillations' are only present for very small absorption coefficient values (k). d_p is of the order of 1 µm. For bulk materials under the condition that $\ell \gg d_p$, this effect is very small. The condition is that

$$\ell > \frac{\lambda_0}{2\pi n|\cos\phi_i|} \tag{4}$$

where ϕ_i is the incident angle used (45° here) and n is the refractive index.

Thus, in our case, for bulk-like behaviour $\ell \gg 0.450$ µm. Since our film thicknesses are 10–20 µm, it is very unlikely that the effective thicknesses effect is relevant.

Of course, the effect of any 'special' surface electric field can, at least in principle, be checked using a transmission experiment. We have tried to do this for several of the polymers studied here. At ~1% level the water band is extremely weak, while at ~12% it is extremely intense (for say a 20 µm film). It is thus very difficult to collect a meaningful intensity value by transmission. Nevertheless, we have been able to compare, to a first approximation the ATR and transmission spectra of a S8 saturated film, removing the excess surface water by a 'patting' procedure. The result, given in Fig. 6, clearly indicates that the 'perturbation' is roughly the same for both electronic field arrangements. It is unlikely that our $\underline{P}$ factors are due to water accumulation in the evanescent field.

4.3. The effects of vibrational coupling

It is well-known [28,32,63] that the extremely broad vibrational profiles exhibited by the ν(OH) (or ν(OD)) bands of H_2O (or D_2O) are associated, to some extent at least, with the effects of intra-molecular coupling of the two stretching modes of the water molecule. Furthermore, because of very strong (coupled and co-operative) motions of the hydrogen-bonded water molecules (in a polymeric network), intermolecular coupling effects result in a 'collective' contribution [54,56] to the ν(OH) band profile. For Raman 'modes' (bands) this phenomenon has been exploited [32,43] to give a quantitative measure of polymer–water interaction. It is clear that these two effects may cause an intensity distribution behaviour (Fig. 7) which is virtually unique in IR spectroscopy. In order to avoid such complications, we have used a D_2O/H_2O mixture (4% D_2O) in order to isolate the OD oscillator

$$H_2O + D_2O \rightarrow 2HDO; \quad K_{eq}^{295} \cong 4.0 \tag{5}$$

using HDO production. Both intra-molecular and inter-molecular coupling are removed [43] and the effects on the band shape are clearly demonstrated in Fig. 7. The effects of isotopic dilution [41,62,63] include a dramatic reduction in band width (Table 2) and an associated simplification of the

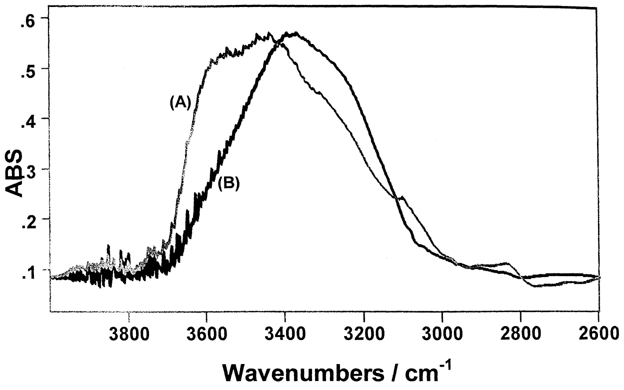


Fig. 6. Comparison of ATR (B) and transmission data (A) for a 10 µm film for S8 polymer saturated (12.7%) with water. The 'absorbance' scale is common to both spectra.

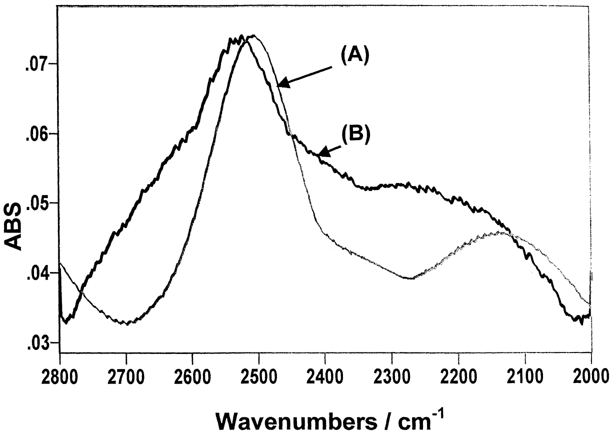


Fig. 7. The effects of isotopic dilution in the ν(OD) band of a D_2O (4%) H_2O mixture in S8 polymer. (A) ν(OD) band of HDO in liquid D_2O(4%)/H_2O mixture. (B) ν(OD)/band of HDO in the polymer.

band shape. We have determined $\underline{P}$ based on Eq. (1) with concentration adjusted for the equilibrium represented by Eq. (5). The results are included in Table 1. It is seen that the $\underline{P}$ values are somewhat greater for the decoupled water molecules HOD than for D_2O (or H_2O) molecules. The possible significance of this result is discussed below. But it is clear that the high extinction coefficients are not solely due to 'collective mode' intensity, nor to delocalised 'OH' motions, nor to intramolecular coupling.

4.4. The effects of 'percolation' processes

There have been a number of investigations [64–66] of 'percolation' based processes in polymeric materials, mainly connected with the calculation or simulation of percolation thresholds for drug-release from porous media. However, the direct measurement of transport coefficients with fractal dimensions in porous media does not seem to have been reported in the polymer literature, possibly because 'pore' design and/or control is difficult. It is unlikely therefore that 'collective' water transport phenomena in polymers could be detected using vibrational spectroscopy, especially for systems without any control of pore distribution.

Table 2
Comparison of band positions and widths of ν(OH) and ν(OD) bands of water, both coupled and decoupled vibrations

	Pure water		Water in SPEES/S_8	
	Position (cm^{-1})	Width (cm^{-1})	Position (cm^{-1})	Width (cm^{-1})
$\nu_{(OH)}$ H_2O	3200–3500	~450	3200–3600	~450
$\nu_{(OD)}$ D_2O	2400–2600	~300	~2500	~320
$\nu_{(OH)}$ HDO (4%D_2O)	~3400	~350	~?	~?
$\nu_{(OD)}$ HDO (4%D_2O)	~2500	~230	~2550	~230

4.5. The effect of water–polymer molecular interactions

Because the ν(OH) (or ν(OD)) bands of liquid water are sensitive primarily to water–water OH–O interactions (and collective) dynamics, it is not obvious from such profiles (nor with their change as a function of sorption [1–3,34,42]) that strong water–polymer interactions are formed. There are, however, sometimes obvious markers for such interactions. Two particular ones are found in this work are shown in Figs. 8 and 9. The wider literature demonstrates that normal modes of a number of chemical groups (notably –C=O, C=N, SO, NO_2, etc.) may shift and intensify when hydrogen bonding takes place in liquid mixtures [6,7,16,17] or in thin films [67,68] or at interfaces [69]. But relatively little work of this kind has been published for polymeric functional groups. Nevertheless, there is good evidence from a variety of sources that water–polymer hydrogen-bonding does occur [28–47,70,71]. Fig. 9 potentially provides a detailed 'snapshot' (over the first 20 min of water sorption) of the changing polymer–water interactions as water enters the 'free volume' (defects, microvoids, etc.) in the polymer matrix. It is clear that the shift of the ν(*C=O*) band of PET is due to such interactions. Fig. 10 shows that strong water interactions with the polymer surface occur at 3–4 min into the sorption process and again at about 20 min. We interpret this to mean that between the two

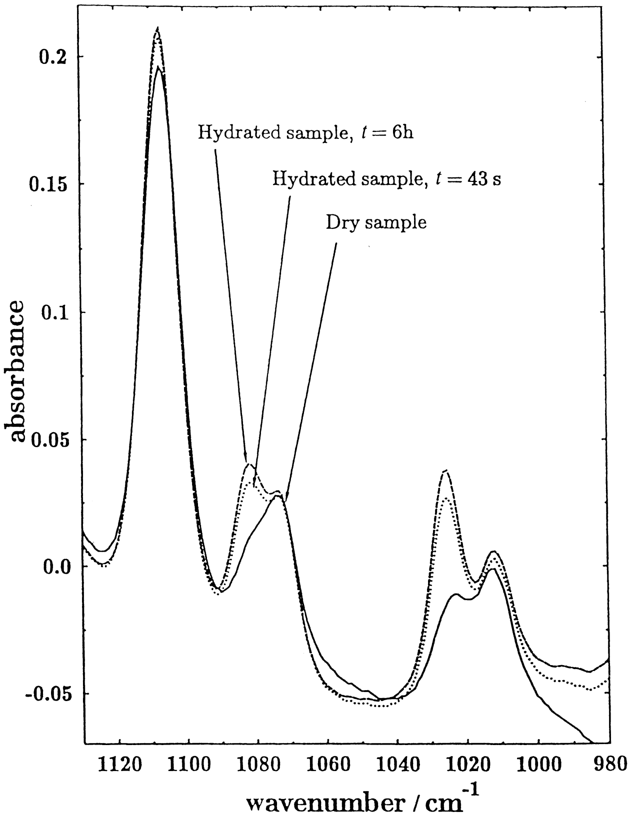


Fig. 8. The IR $\nu_s(SO_3^-)$ band of PES (S5) before and after hydration showing strong polymer water interactions. (Reproduced, from Pereira M, PhD Thesis, Durham University, 1994.)

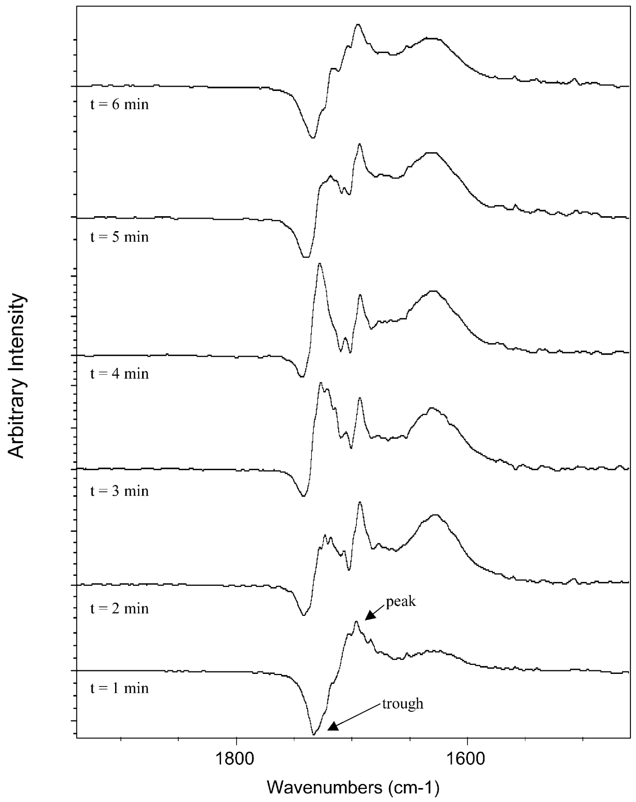


Fig. 9. FTIR/ATR of the ν(C=O) band of PET as a function of water content. $T = 1$ min at bottom in 1 min intervals up to $t = 6$ min. Band shifts and shapes are elucidated in the text.

abrupt increases in $\nu(C{=}O)$ shift (from the original $\nu(C{=}O)$, 1720 cm^{-1} band position) water is filling the voids and interaction with the polymer C=O groups is relatively less important, compared with the times when the voids are either almost empty or completely full. Thus, IR spectroscopy is able to provide a method of monitoring polymer–water interactions at the polymer interface in real time and on a micron or sub micron scale. Most treatments of functional group–water interactions in polymers employ the classical electrostatical approach (see Ref. [27], p. 16–35 for the general approach adopted, and Ref. [72] for a recent survey of work on polymers]. These do not include the contributions to the covalency induced by donor–acceptor (i.e. charge transfer) interactions which have been thought for many years [6,15,73] to be important for the formation of vibrational profiles in hydrogen bonded system. Such covalency has been only rarely mentioned recently in the polymer literature [5]. However, modern 'ab initio' computational methods have been applied [74–80] to a wide range of H_2O-chemical group interactions including amides, ketones, ethers and amines. These *do* include the effects of CT and the general conclusions support the original rather crude estimates (see Ref. [6] p. 137) that large infrared intensity perturbations (up to two orders of magnitude [76]) may be predicted using the most accurate intermolecular potentials which we have at the present time.

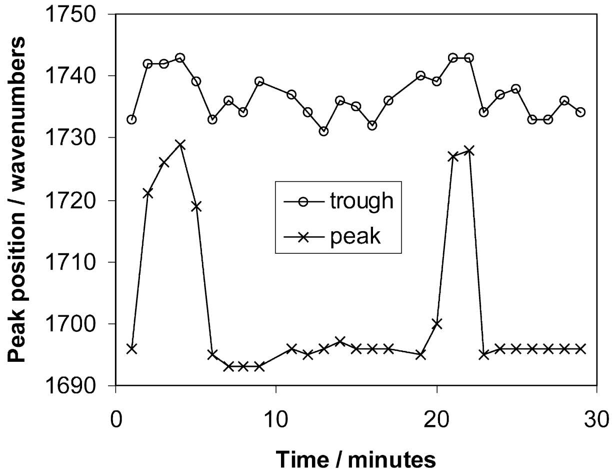


Fig. 10. The complex ν(C=O) band shifts in PET as a function of water content-showing 'peak' and 'trough' variations (from Fig. 9) as a function of polymer–water interactions.

It is therefore not surprising that we have observed rather large $\underline{P}$ values for the water band intensity; these being very much in line with those found [16,17,75–80] for common functional group band intensities when they form hydrogen bonds with H_2O. However, as shown in Fig. 2 the different polymeric functional groups give different levels of perturbation which would normally be expected to scale with chemical group 'polarity' (maybe ionisation potential for charge transfer interactions—see Table 1) or even with hydrophilicity. Fig. 2 shows that such a correlation is not obvious. So, for example, the (relatively) hydrophobic PVC and the (relatively) hydrophilic PET show the same perturbation whereas the SPEES/PES polymer electrolytes [50] show decreasing $\underline{P}$ values for increasing levels of SO_3^- functionality. Clearly, the chemical details do not control these deviations from Beers Law. Rather, it appears that proximity to the surface is much more important. Fig. 2 shows a reasonably good correlation with the water content. Obviously, the lower the equilibrium level of water the closer (on average) water molecules reside to the interaction surface. Since the quantum mechanically based, electron Donor–Acceptor (D/A) interactions [15] have a very much shorter distance range ($\sim R^{-12}$) than the classical Coulombic ($\sim R^{-6}$) forces of attraction (Ref. [6] chapter 1), such a result adds credibility to the hypothesis that it is the 'covalency' which leads to the large water intensity perturbation. More work is clearly needed on other polymers (e.g. hydrogels) where the activity of water can be varied and controlled more easily. However, it appears that a (reasonably accurate) IR intensity measurement can be used to predict the water content of a polymeric material, although chemical structure is always a possible secondary factor.

5. Summary and conclusions

The large intensity perturbation of the 'IR ν(OH)' band profile (both coupled H_2O, D_2O or decoupled – HDO) at equilibrium sorption of a variety of polymers is shown to be caused by strong polymer–water interactions. The elimination of other possible sources of extinction coefficient enhancement has been discussed and such sources have been discussed on scientific grounds consistent with current literature. This strong deviation from Beers law correlates well with the concentration of water (at equilibrium) and therefore with the proximity of the water molecules (on average) to the perturbating surface. This leads to us to conclude that short ranged D/A interactions (resulting in polymer–water covalency) are important. Chemical specificity is clearly a factor too but is less obviously a perturbation source. This may be because the longer-ranged Coulombic forces are less discriminatory, and lead to similar interaction energy for a whole range of chemical groups.

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