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FTIR–ATR studies of the sorption and diffusion of acetone/water mixtures in poly(vinyl alcohol)

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Abstract

The diffusion kinetics of water and acetone into dried PVOH polymer films have been measured simultaneously using the FTIR–ATR technique. The data have been fitted to a pseudo-Fickian model, along with allowance for a 'lag' time which lengthens considerably when the water mole fraction is low. It has been found that a case II model is viable at short times when the polymer is 'glassy' ($<T_g$). However, as water enters the polymer (unzipping the chain–chain hydrogen bonding), conversion to a 'gel' is rapid and the crystallinity drops concurrently. A Fickian-like model then becomes viable at intermediate times. FTIR–ATR is an excellent technique with which to study sorption from solvent mixtures. In this case, for example, we have demonstrated that acetone does not enter a dry polymer film and that the micro-crystallinity of the PVOH returns at longer times. Neither of these two potentially important results could have been obtained using gravimetric methods.

Keywords: Polymer; Diffusion; Infrared

1. Introduction and background

Poly(vinyl alcohol) is a water soluble polymer which forms hydrogels [1] very readily. It is also biocompatible and biodegradable, and is widely used in medical, cosmetic and packaging applications [1,2]. Furthermore, it is the material of choice for construction of pervaporation membranes, for water removal or for vapour permeation/ separation systems. In the latter connection, there has recently become an awareness of the importance of PVOH/ clay nanocomposites [3–7] for the potential modification of barrier properties of such membranes. The sorption and diffusion properties of PVOH and its composites are, therefore, of considerable interest from both a fundamental and practical point of view. With this in mind, we have explored the sorption and diffusion of water (and its mixtures with acetone) in coherent, thin films of PVOH and some clay nanocomposites of PVOH by FTIR–ATR spectroscopy. Initial work on the latter materials was published previously [6]. In doing so, we attempt to add understanding in the following areas:

1. The behaviour of PVOH based materials towards ingress of water, and it's mixtures with organic polar solvents.
2. The interactions between water and acetone and the influence of such interaction (if any) on the transport/ barrier properties of the polymer.
3. The effects of nanocomposite formation on the sorption and diffusion of water and/or mixed solvents.

This paper describes the work on PVOH itself, while a following paper will address a detailed study of the composite materials we have studied [7].

As a starting point, it is useful to briefly review the current understanding of water/acetone interactions and the state of water in PVOH from previous work. There is a small, but growing, literature on the state of water in hydroxylated (and, therefore, hydrophilic) polymers. The number of 'states' of water in PVOH has always been found to be two or three depending on the water concentration, the temperature regime and the technique used. The thermal transitions measured by DSC have generally led to the conclusion that three states of water exist above a water content of about 30% [8–12]. These are bulk water, freezable but weakly bound water (fpt < 0 °C), and (by implication) 'non-freezable' (strongly bound) water. This 'non-freezable' water—which breaks up the intra and inter-chain hydrogen bonding of the polymer—has been established [13,14] quantitatively by DSC. Two interacting

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populations of water molecules (weakly and strongly interacting 'water' molecules) have also been observed in the IR at 3400 and 3280 cm^{-1}, respectively. Several attempts have been made to elucidate the 'segregation' of water at different places in the polymer matrix. In particular [9,11], the segregation of water in the amorphous phase during crystallisation may mean that water cannot crystallise (below a particular 'critical' concentration) before the solvent/polymer system becomes 'glassy'. Changes of 'apparent' T_g are, therefore, important in terms of interpretation, vis a vis non-frozen water. Unanimity is, however, still to be reached about precisely where water resides in the polymer, and the time scale and concentration dependence of such 'residence'. So, the extensive spectroscopic (NMR and PALs) investigations of Hodge and collaborators [15–17] have led to the conclusion that water does not 'inhabit' intact crystallites; but instead contributes to the break down of inter and intra molecular hydrogen bonding. This then gives rise to enhanced polymer 'mobility' (NMR line width [18]). However, the XRD work of Assender and Windle [19] seems to indicate that water molecules might well inhabit the crystalline lattice, at least under some circumstances.

Some very useful work on the breaking of the water 'network' in polymers has been obtained using Raman and infrared spectroscopy by Kitano and co-workers [20–22]. The general conclusion is that the 'collective' bands [20,21] of water (reflecting a tetrahedral, but dynamic, water hydrogen bonding network) are reduced in the presence of polymer chains. This, in turn, reflects a lower long-range order (of water molecules) in a polymeric 'gel' (than in pure water). The 'defect' probability is higher for charged or hydrophilic polymeric chains and lower for neutral polymers. Unfortunately, there seem to be no published data for PVOH. However, it seems likely that a hydroxylated polymer might, through strong polymer–water interactions, disturb the water structure more than for the polymers (PVC, PE, PP, PS, PET, etc.) where water diffusion studies are relatively common. As far as we are aware, there are no reports of liquid water (or mixed solvent) diffusion into PVOH, although there have been reports of water diffusion in other hydroxylated polymers, especially by Zografi et al. [23,24], Migliardo et al. [25,26], Wu et al. [27–29], Yarwood, Sammon et al. [30,31] and Lagaron et al. [32]. These studies mainly involve epoxys, caprolactones or haloses.

In any discussion of the diffusion of a mixed solvent into a polymer film, the solvent–solvent interactions are almost certain to be of relevance. Surprisingly, there have been relatively few detailed studies of the water–acetone interactions and their consequences. Work by Max and Chapados [33,34] and by Schmuttenmaer and Venables [35–37] has summarised recent spectroscopic and molecular dynamics investigations. A full principal components analysis of the FTIR spectra [33,34] has led to deductions about the different water or acetone 'species' (with different numbers of interactions) that are present over the whole concentration range. Although each of such 'species' (with a defined ν(OH) or ν(C=O) band position) is 'well-defined' on the vibrational time scale (molecular dynamic processes on a psec scale [38]), this is not so on the time scale of sorption and diffusion at a polymer interface. Nevertheless, for a given mixture it ought to be possible to discern the principal interactions between the water and co-solvent, and assess the role (if any) of such a distribution of interactions on the diffusion process.

Two principal results arise from molecular dynamics simulations on this system [38]. Firstly, water tends to remain in the water–water 'clusters' up to high acetone concentrations ($x_w < 0.2$). Secondly, the hydrogen bond lifetimes increase in the mixture. As expected, it is the 'cooperative' effects in water that are mainly affected by addition of acetone. Whether such effects are relevant to the diffusion process in PVOH remains an open question. This will be discussed in the light of the diffusion rates found at different water levels in the mixture (Section 4).

2. Experimental and collection parameters

2.1. Sample preparation

Diffusion experiments of water into PVOH were performed on a low molecular PVOH with an average molecular weight of 31,000–60,000 g/mol and a hydrolysation degree of 98–99%. The polymer was obtained from Aldrich and used as received. PVOH films were cast from aqueous solutions containing 1 g of polymer in 20 mL of deionised water. To ensure complete dissolution of the polymer, the solution was heated to 90 °C for 4 h. Films were cast directly onto the ATR crystal, covering the heatable area of the Golden Gate™ ATR cell. Samples were allowed to dry over night at a temperature of 40 °C before diffusion experiments were performed. Samples had a thickness of 26 ± 6 μm which was calculated based on the amount of solution used in the casting and checked by measurements with a micrometer on films dried and removed from the crystal after the acetone/water experiments. The water/acetone mixtures were freshly prepared, by volume, immediately before the experiment.

2.2. Diffusion cell

Diffusion experiments were performed using a Graseby Specac Ltd Golden Gate™ ATR cell with a pressurise-able cell to create an infinite liquid reservoir. A schematic of the cell is shown in Fig. 1.

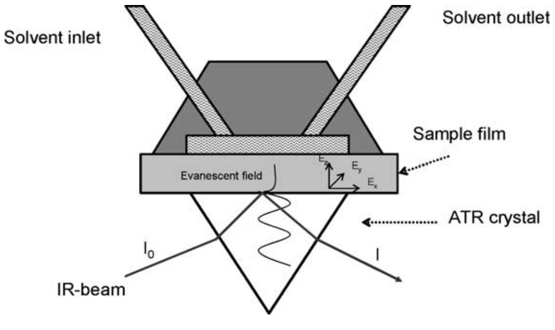

Fig. 1. Schematic set-up of the diffusion cell.

2.3. Collection parameters

The experiments were performed on two FTIR instruments. The temperature was kept constant at 40 °C throughout the experiment unless otherwise stated. The data on water diffusion was collected on a Thermo Nicolet Magna 860. Spectra were collected as an average of 10 scans at a resolution of 4 cm^{-1} and saved as single beam spectra. For the analysis, these single beam spectra were ratioed either against a single beam spectrum of the clean crystal or against the single beam spectrum of the dry film. Later experiments were performed on a newly-acquired Thermo Nicolet Nexus instrument. On this instrument a series of spectra could be collected with just one scan, making collection of data in the early stages of the experiment more accurate. Apart from the changes in the number of scans per spectrum, all other parameters were kept the same. Samples for these experiments were still dried over night at 40 °C and then allowed to equilibrate at the desired temperature for 40 min before the start of the data collection.

Diffusion of water/acetone mixtures proceeded at a slower rate, necessitating longer experiment durations while time between the collection of spectra was increased. Data was collected with 10 scans per spectrum at a resolution of 4 cm^{-1} on the Thermo Nicolet Nexus instrument.

3. Treatment of data

3.1. Obtaining peak areas

Special considerations of data treatment apply to the reliable derivation of diffusion kinetics from the water/acetone phase into a hydroxylated polymer such as PVOH. These are necessary because of the potential complexity of the ‘system’ under exploration; viz. the different processes which can simultaneously occur during the sorption and diffusion process. These include:

(a) Diffusion of water and/or acetone (cooperatively or separately?).
(b) Gel formation and swelling of the polymer (and concurrent changes in ‘crystallinity’).
(c) Hydrogen bonding of water and/or acetone to PVOH (and to each other).

All three of these processes affect the FTIR spectra in a profound way and are not easily separated. Furthermore, there could be effects (on the band shapes for example [39]) due to rapid exchange of water and polymer protons (but probably too slow to have a very significant effect). A very careful approach to spectral collection band choice and integration was, therefore, needed if meaningful data were to be obtained. The question is how spectra like those shown in Fig. 2(a). should be integrated one needs to reliably capture the diffusion

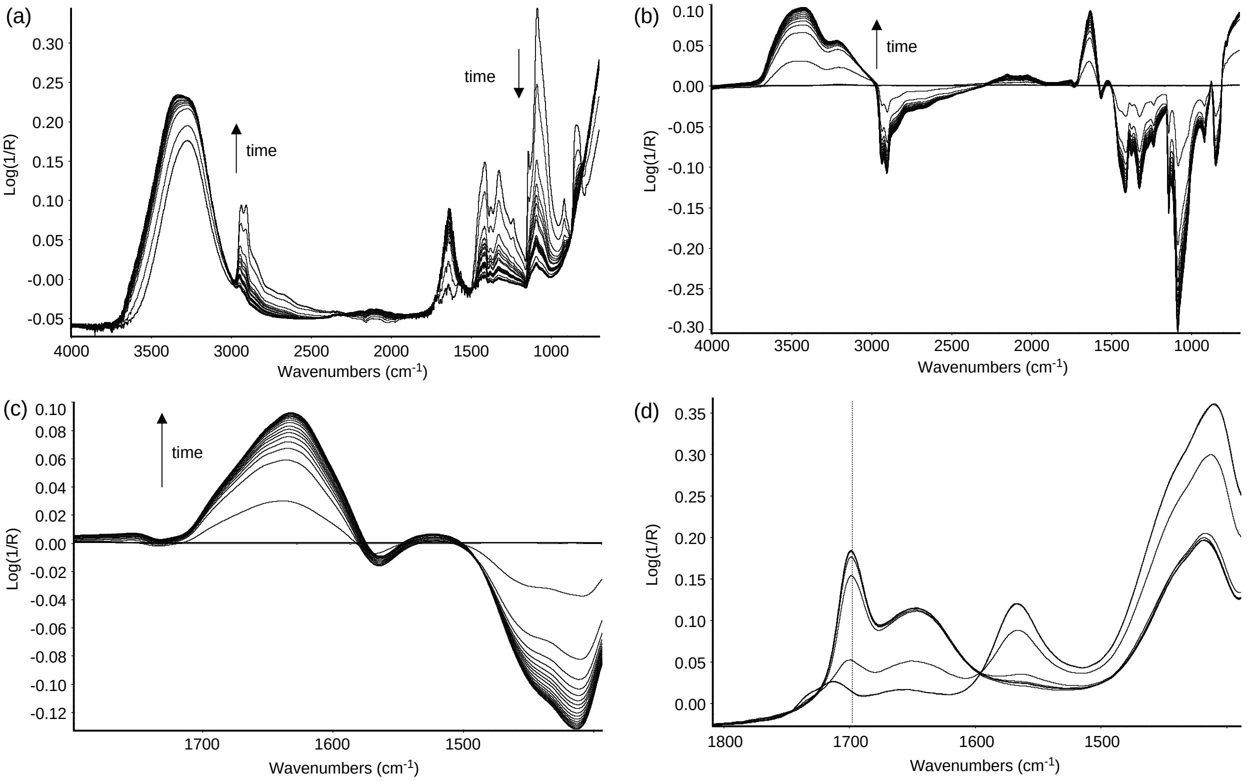

Fig. 2. (a) Spectra of diffusion of water into PVOH (as collected); (b) difference spectra of diffusion of water into PVOH (dry film subtracted); (c) difference spectra of diffusion of water into PVOH (dry film subtracted) in the region of 1800–1400 cm^{-1}; (d) spectra of diffusion of acetone/water mixture (molar ratio 1:1.76) into PVOH in the region of 1800–1400 cm^{-1}.

of both water and acetone in the presence of the polymer (whose crystallinity and effective T_g is changing with solvent penetration, commensurate with the formation of a gel). Often our experience has been to use the dry polymer film as a 'background' so that the log(1/*R*) value of zero can be used as a point of reference, with features above this relating to the diffusing media and features below being associated with the swelling polymer matrix. This is shown in Fig. 2(b) and as may be observed the ν(OH) region of the spectra was severely complicated by changes in water concentration, water–polymer interactions and polymer swelling, but is still somewhat easier to understand than Fig. 2(a). Changes in the intensity of the ν(OH) band of the polymer due to swelling of the polymer could be responsible for the relatively weak band in the ν(OH) region of the difference spectra. The δ(OH) region is less influenced by this effect since the polymer does not exhibit a strong δ(OH) band. After considerable effort, it was found that use of the water bending band δ(OH) (near 1640 cm^{-1}) was the most reliable procedure (Fig. 2(c)).

This band is less sensitive to (chemical) 'environmental' effects than the ν(OH) band and is not overlapped by a δ(OH) band arising from the polymer. Integration of this band (as seen from Fig. 3) gives a smooth (and reproducible) diffusion curve. Peak area measurements for changes in the δ(OH) band due to water ingress were obtained by integration of the difference spectrum. In the case of acetone/water mixtures the acetone diffusion was measured using the well-known ν(C=O) band at ~1700 cm^{-1} (Fig. 2(d)). Overlapping of the ν(C=O) band of acetone and the δ(OH) of the water requires deconvolution of the peaks by means of peak fitting. To obtain area measurements for the ν(C=O) and δ(OH) bands during the diffusion of acetone 4 mixed Gaussian and Lorentzian peaks were fitted in the region between 1800 and 1400 cm^{-1} of the spectra. The values obtained for the first (dry film) spectrum of each run were subtracted from the subsequent values to plot the diffusion data and determine diffusion parameters. Since the ν(C=O) band of acetone is overlapped by a ν(C=O) band arising from acetate residue of the unhydrolised polymer, the value subtracted for the ν(C=O) band is slightly over compensated once the polymer starts to swell due to ingress of water. This results in small negative values for the area of the ν(C=O) band after the area of the δ(OH) band started increasing (Fig. 4).

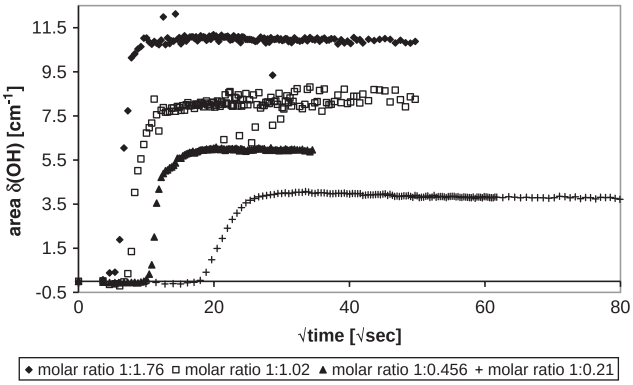

Fig. 3. Diffusion of the water fraction of acetone/water mixtures into PVOH as a function of √time for various molar ratios.

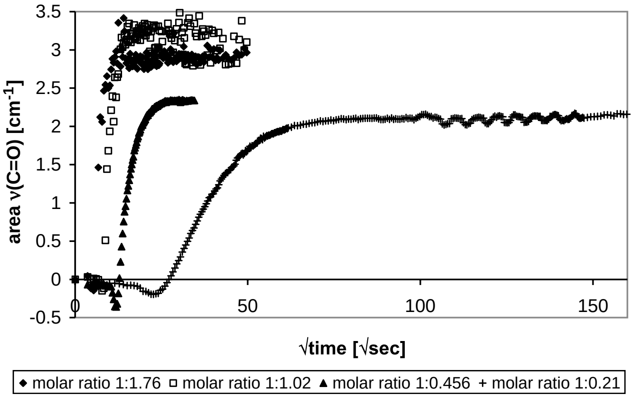

Fig. 4. Diffusion of the acetone fraction of acetone/water mixtures into PVOH as a function of √time for various molar ratios.

3.2. Modelling of diffusion data

Data fitting to a suitable model is clearly required to derive a quantitative measure of diffusion kinetics from the experimental curves shown in Figs. 3 and 4. Several possibilities have been tried. These include a purely Fickian (case I) model [40–42] (usually recommended for a 'rubbery' polymer above its T_g). In that case

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right] \tag{1}$$

where, M is the mass absorbed at a time t and equilibrium, respectively, D is the diffusion coefficient, L is the film thickness, which using the ATR approach, becomes (as described in [42])

$$\frac{A_t}{A_\infty} = 1 - \frac{8\gamma}{\pi[1-\exp(-2\gamma L)]} \times \sum_{n=0}^{\infty} \left[\frac{\exp\frac{-D(2n+1)^2\pi^2 t}{4L^2}\left[\frac{(2n+1)\pi}{2L}\exp(-2\gamma L) + (-1)^n(2\gamma)\right]}{(2n+1)\left(4\gamma^2 + \frac{(2n+1)\pi}{2L}\right)} \right] \tag{2}$$

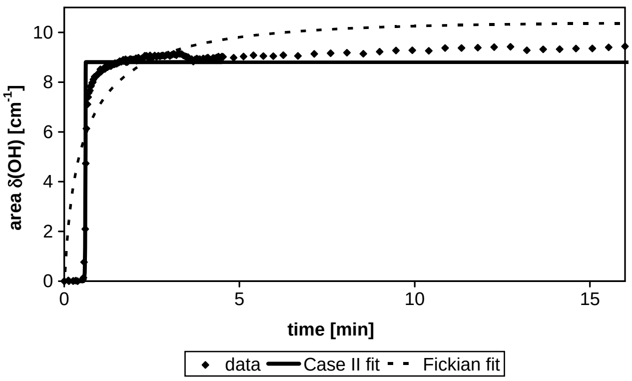

Fig. 5. Case II fit and experimental data for diffusion of water into PVOH.

where A_t and A_∞ are the spectral absorptions at a time t and equilibrium, respectively, and d_p is the penetration depth, $\gamma = 1/d_p$, D is the diffusion coefficient, L is the film thickness.

We also explored the case II model [41,43–46], usually employed for the penetration of a solvent front into a 'glassy' polymer. In that case the absorbance ratio is

$$\frac{A_t}{A_\infty} = \frac{1-\mathrm{e}^{2\gamma \nu t}}{1-\mathrm{e}^{2L\gamma}} \qquad (3)$$

where ν is the diffusion front velocity, $\gamma = 1/d_p$, L is the film thickness.

As we have found previously [6,47–49], for other polymer systems, neither Eq. (1) nor (2) gave a very good fit to the data over the whole timescale of observation, as illustrated by the current data for diffusion of water into PVOH (Fig. 5).

Table 1
Diffusion coefficient and 'delay times' for PVOH

Acetone/water ratio	Water		Acetone	
	Intercept/L (min/μm)	Diffusion coefficient D (cm^2/s)	Intercept/L (min/μm)	Diffusion coefficient D (cm^2/s)
Pure water	0.02	6.7×10^{-5}	–	–
1:1.76	0.02	1.1×10^{-4}	0.02	2.0×10^{-5}
1:1.02	0.03	6.8×10^{-5}	0.06	1.1×10^{-5}
1:0.466	0.07	2.4×10^{-5}	0.11	1.1×10^{-6}
1:0.21	0.23	1.6×10^{-5}	0.61	3.9×10^{-8}

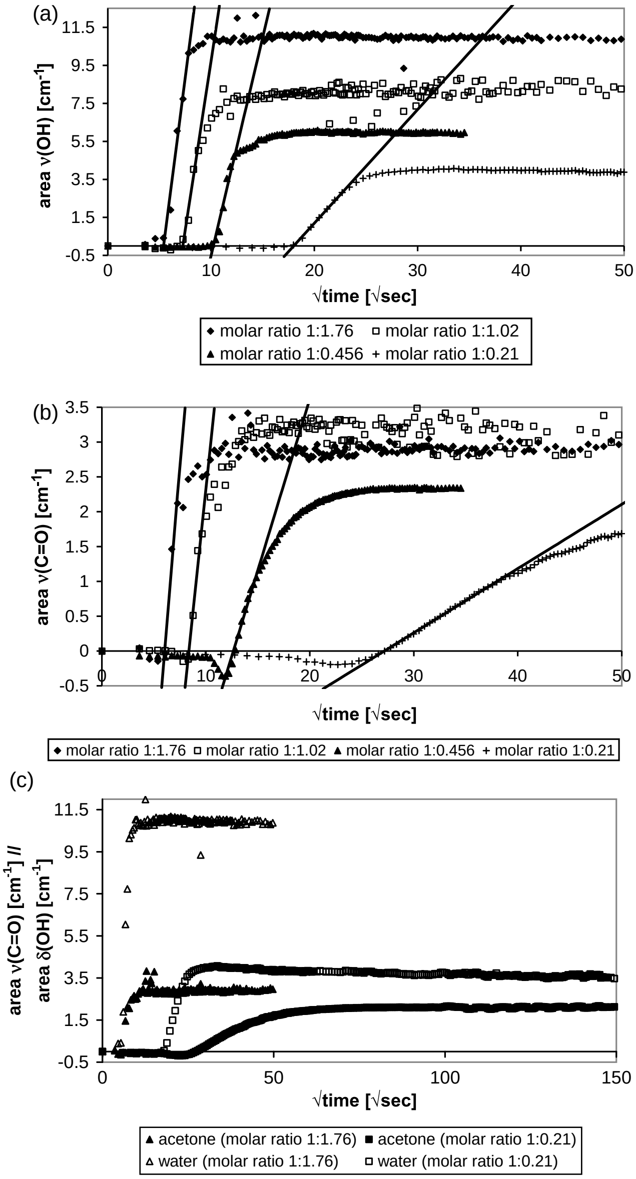

Fig. 6. (a) Comparison of initial slopes for diffusion of the water fraction of acetone/water mixtures into PVOH for various molar ratios; (b) comparison of initial slopes for diffusion of the acetone fraction of acetone/water mixtures into PVOH for various molar ratios; (c) diffusion of acetone/water mixtures with molar fractions of 1:1.76 and 1:0.21 into PVOH.

A large effort has been made in the last 10 years to develop viable models for the derivation of relevant parameters with which to characterise the sorption, diffusion and permeation of liquid penetrants into (and through) polymer films. These have included approaches based on diffusion driven by a concentration gradient [50,51] or by intermolecular forces [52,53] (plus a resistance to flow). Models have included plasticisation and swelling driven stress (and cracking) [54], and both time and concentration dependent diffusion coefficients [55]. In many cases, due to changing polymer morphology during the penetration process, a mixture of Fickian and case II processes needs to be used. So the exponent n (Eq. (4)) has been found to be in the $n = 0.6$–0.8 range (usually referred to as 'anomalous' diffusion) [56]. There has been discussion of 'lag' times (followed by accelerated uptake) and their causes [57]. In particular, the resulting sigmoidal shape of the diffusion curve [55] (Figs. 3 and 4), which can sometimes be mistaken for the necessity of using a case II model has received attention. Relatively little has, however, appeared on the sorption or diffusion of liquid mixtures into polymers. However, Barbari et al. [58] have used infrared spectroscopy to study simultaneous diffusion of a ketone and alcohol into polyisobutylene. A review of earlier work on models used for liquid diffusion in polymers was given by Rossi [59].

In the past, we have employed a 'dual' mode model [47–49]. In reality, this is a sum of Fickian processes for two populations of molecules which are assumed [41,43,44] to have independent Fickian transport behaviour. Such a model often fits the diffusion curve quite well, without necessarily leading to a very satisfactory interpretation of the two parallel processes on which the model is built [41,43,44,47–49]. In this work, we have considered an alternative approach based on an observed initial 'lag' time (normalised to path length L), during which little sorption apparently occurs (at least within the evanescent field), followed by a pseudo-Fickian ($\sqrt{t}$ power law) behaviour predicted [42] from Eq. (1) at short times, viz.

$$\frac{M_t}{M_\infty} = \frac{2}{L}\left(\frac{D}{\pi}\right)^n t^n, \quad n = 0.5 \qquad (4)$$

This approach is shown in Fig. 6(a) and (b) and the resulting parameters are given in Table 1 as a function of water mole fraction and acetone: water molar ratio. As may be seen from Fig. 6, fits to Eq. (3) (case II) are prone to large deviations in the intermediate time regime.

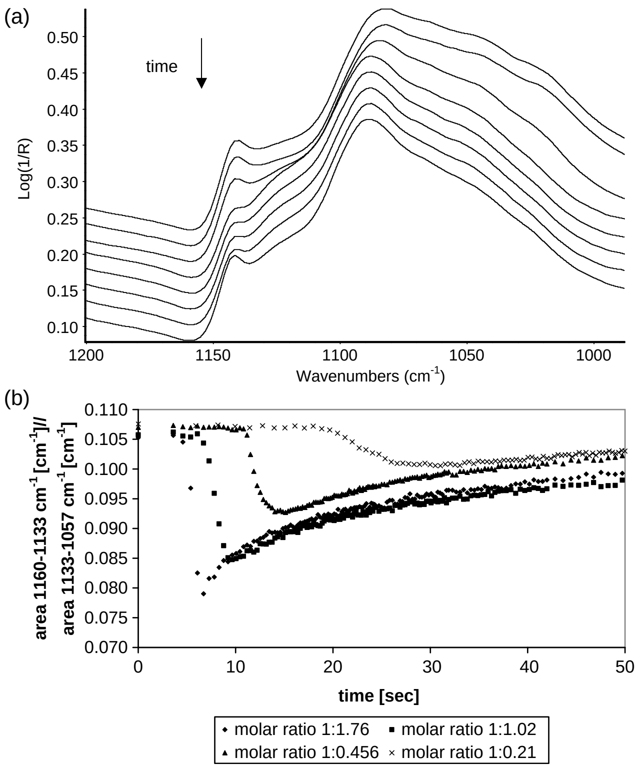

Fig. 7. (a) Changes in the 1200–960 cm^{-1} region during diffusion of acetone/water mixture with a molar ratio of 1:1.76 into PVOH; (b) changes in crystallinity during diffusion of acetone/water mixtures into PVOH.

4. Results and discussion

4.1. Diffusion data

A summary of the data obtained from curves such as those shown in Figs. 3–6 is given in Table 1. For the acetone/water mixtures studied here, the use of a pseudo-Fickian model (Eq. (4)) has the disadvantage of being unable to deal with 'plasticisation' effects (in this case formation of a polymer gel), caused by ingress of water. Nevertheless, we felt that this was preferable to employing a case II model, which is supposedly relevant for a 'glassy' polymer. Since the T_g of PVOH is reported [16] to be near ambient temperature for a water content of 10–16 wt%, we expected that chain flexibility would be reasonably high for the temperatures studied. This is reflected by the significant reductions in crystallinity measured at higher water contents (Fig. 7(a)) using the ratio of bands at 1096 and 1140 cm^{-1}, as described in the literature [60,61].

It is clear from Figs. 4 and 6 and Table 1 that the diffusion of both water and acetone into PVOH depend quite sensitively on the water/acetone mixture. In particular:

1. Pure acetone does not diffuse at all into a dry PVOH film—or, at least, no diffusion can be detected by FTIR–ATR. Acetone does dissolve, however, into a moist film, doing so by a Fickian mechanism (Fig. 8). This moist polymer was obtained by forming a film at room temperature overnight with neither temperature nor humidity control.
2. As the proportion of acetone in the mixture increases, the diffusion rates for both water and acetone decrease. So acetone inhibits the diffusion of water into the film. This is measurable both from the 'lag' time and the diffusion rate parameters.
3. The diffusion rate of acetone is always lower than that of water, even at the higher water concentrations.
4. The diffusion curves for water and acetone are more similar at relatively high water concentrations, but become clearly separated, and vary in overall shape (Fig. 6(c)) as the acetone content increases.
5. The amount of water in the evanescent field must be approximately 50% of the band intensity at equilibrium before acetone is detected.

These effects point unequivocally to the need for PVOH to contain water (or moisture) before acetone will enter the matrix. In view of the ability of acetone to form hydrogen bonds with PVOH and in view of its high polarity (and expected hydrophilicity—after all, acetone mixes with water in all proportions) this may seem surprising. This experimental

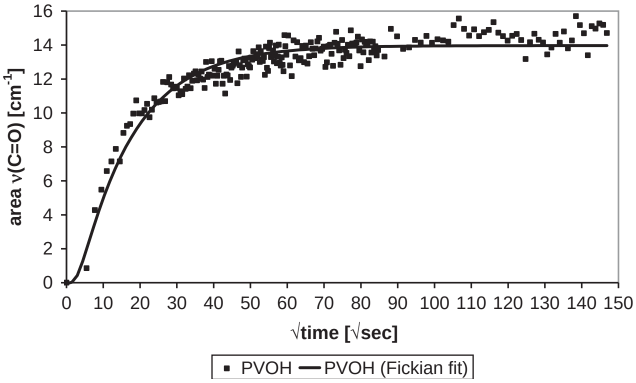

Fig. 8. Data for acetone into a PVOH film that had not been rigorously dried at 40 °C.

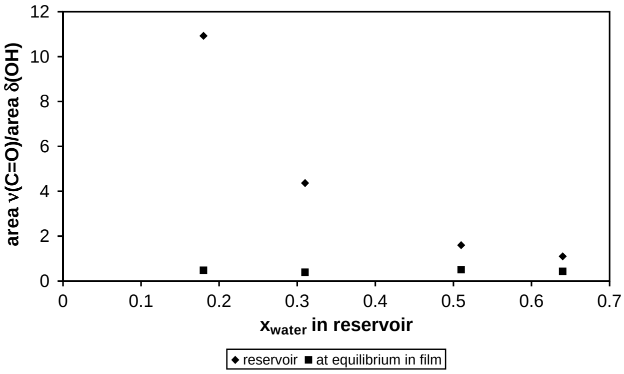

Fig. 9. Ratio of the areas of the carbonyl stretch and the hydroxyl bend for various acetone:water mixtures in the reservoir and in the film at equilibrium.

result points to the very strong inter-chain hydrogen bonding of PVOH. It would appear necessary that such very strong hydrogen bonds need to be broken before acetone can enter the inter-chain voids and that unlike water, acetone is not capable of breaking them. Stated another way, acetone is 'soluble' in water but not in dry PVOH. Nevertheless, acetone is soluble in water just because of C=O···H–O–R hydrogen bonding. It seems clear that this low molecular weight polymer displays a 'co-operativity' of polymer–polymer intermolecular forces which prevents such interactions, unless water is present. The network forming and small sized water molecule is thus able to 'unzip' the polymer–polymer interactions (as is already known [10,12–17]) and allow larger molecules to penetrate the extremely hydrophilic system. Such effects are relevant and important in both pharmaceutical [24,62] and biological [63] systems, and are frequently quoted as a requirement; for example, for drug transport.

The question now arises as to whether 'complexes' formed in water/acetone mixtures (at different proportions in different mixtures [33–37]) are relevant to the sorption and diffusion of such mixtures into polymeric materials. It is interesting to compare the sorption levels and spectra of the water and acetone moieties during the experiment. It would appear (Fig. 9) that the ratio of acetone:water at equilibrium in the polymer film is (relatively) independent of that ratio in the liquid mixture. Thus, the polymer film 'structure' (via hydrogen bonding interactions between the chains) controls the take up and the relative amounts of the two solvents. Furthermore, although the acetone ν(C=O) band shows a small shift (2–3 cm^{-1}) to lower energy in the film (as compared to with the liquid mixture), changes in the acetone environment, across the concentration range and over the time scale of the experiment, are minimal (Fig. 2(d)). Thus, although the acetone shows evidence of stronger hydrogen bonding in the film there is little or no evidence for changing water–acetone or PVOH–acetone interactions. This implies either a fixed stoichiometry/structure (see below [33,34]); and, therefore, an acetone environment (in the film) which is independent of changing water concentration in the reservoir. Since the water and acetone are certain to share (to some extent) polymer 'voids' this seems unlikely. The alternative is that our band shapes do change but that the changes are not discernable at 4 cm^{-1} resolution!

Max and Chapados have recently published a summary [33,34] of the 'complexes' which might be expected in a given acetone: water mixture. The distribution is necessarily complicated, but does emphasize that, at a given ratio of solvents, many different interaction types exist (at least in the reservoir). It should be noted, however, that such a distribution is 'dynamic' in nature, and arises only because of the extremely short time scale of the IR technique (compared with that of the diffusion process). The issue of whether the strong water interactions with acetone cause the two solvents to be 'linked' into the diffusion process remains to be explored further (possibly opening up the design of more effective 'solvent' mixtures). However, what is clear (Fig. 9) is that the equilibrium ratio of acetone:water is the polymer always appears to be approximately constant, regardless of the starting ratio. To that extent at least the diffusion of the two solvents may be linked, at least at high water contents.

4.2. Swelling and crystallinity changes

As discussed in Section 3 and shown in Fig. 6 the case II model (Eq. (3)) of sorption kinetics seems to fit the infrared data only at very short times. Since this model is usually [46] employed to describe the diffusion of a solvent 'front' into a glassy polymer, the obvious implication is that the dry polymer is indeed 'glassy' (i.e. is below the T_g) and, as already known [16,60,61], contains substantial proportions of crystalline domains. One advantage of an infrared sorption experiment is that, for an atactic polymer (normally expected of commercial samples) the 1141 cm^{-1} band [60,61] (Fig. 7) can be used to monitor 'in situ' changes of polymer crystallinity. The band ratios D^{1096}/D^{1141} measured are shown in Fig. 7(b). From these data it can be seen that the crystallinity level drops rapidly as water enters the polymer (in contradiction to what was reported by Peppas [61] but in agreement with Hong et al. [64] who showed a decrease in crystallinity in PVOH gels as the water concentration was increased). This is the reason why the polymer becomes rapidly rubbery and why the relevant sorption model quickly switches to a more Fickian time dependence. Inevitably, there will be a 'conversion' between models at intermediate times. However, detailed plots of the behaviour of the band ratio (Fig. 7(b)) show that there is apparently a recovery of the 'crystallinity' (as measured by the 1141 cm^{-1} band) at longer times. This may be due to reorganisation of the polymer chains in the (swollen) 'gel' resulting in the re-forming of microcrystalline domains. The origin of such an effect is not currently understood but seems real and consistently observed from Fig. 7(a).

We have examined the possibility that the ratio D^{1096}/D^{1141} might be affected by underlying acetone bands (which would, however, give a decreasing ratio at longer times) or by the narrowing of the ν(C–O) band at ~1140 cm^{-1} as a result of gel formation [65]. These effects are insufficient to cause the rise in (this measure of) 'crystallinity' shown in Fig. 7(b). This phenomenon might be caused by one of several possible mechanisms. What is clear, however, is that the effect does not occur when sorption occurs from pure water. Here the band at 1141 cm^{-1} disappears when water is introduced and there is no indication of re-forming crystals in the spectra of the PVOH gel. The acetone is, therefore, implicated, but in a way that apparently does not affect the hydrogen bonding at the 'C=O' part of the molecule. One possibility is that acetone–PVOH 'hydrophobic' interactions cause water to be ejected from polymer pores (thereby allowing the re-establishment of interchain hydrogen bonding). Such an effect, known as 'syneresis', is well-known [66,67] in other polymeric gel phases. The driving force for such a process is unlikely to be enthalpic since the water–PVOH interaction is surely of greater energy than that between acetone and PVOH.

Indeed, since the solvation 'free' energy of a methyl group (by water) is very small (and even repulsive under some circumstances [68]) the extent of polymer/acetone 'hydrophobic' interaction is small. However, there could be an acetone–polymer (CH_2) interaction—mainly via dipole induced dipole or dispersive potentials. Whether these are sufficient to release water from the polymer is not clear. Nor is it clear whether 'entropic' drivers; vis a vis the relatively high entropy of liquid water as compared with small, directionally bonded water 'clusters' (in the polymer voids) could be of significant influence. Whatever the energetics of this return to partial crystallinity, it remains an opportunity in terms of the use of gel-producing materials for the construction of dry release 'tablets'. There are clearly diffusion control mechanisms afforded by such materials at different water contents. One might conceivably control release rates by controlling the degree of crystallinity, for example, by pinning the structure in place in a laminate structure. It may also be attractive to maintain a constant 'organic molecule' concentration close to the polymer water interface for controlled sustained release.

Clearly, more detailed work is needed to understand the data of Fig. 8(b). We are, however, confident that the phenomenon is real and that microcrystalline domains are re-entering the evanescent field as saturation is approached. The apparently 'universal' level of final 'crystallinity'—independent of mixture concentration may be correlated with the common concurrent ratio of acetone/water in the films at equilibrium. Further exploration of microcrystallinity in hydrogels would certainly be worth-while.

5. Summary and conclusions

FTIR–ATR is able to provide a wealth of information about the kinetics and interactions relevant to water sorption. In particular the following new information has been derived from these measurements.

Although PVOH swells rapidly and forms a gel at modest water concentrations, the dried material is relatively highly crystalline and initially (for up to 6 min) resists the entry of water. Indeed, the data are consistent with case II diffusion kinetics at very short times.

As water enters the polymer, the material T_g drops rapidly until it is certainly below the temperature of our experiments. The diffusion kinetics become Fickian (or near Fickian), even at intermediate times. The data can be accounted for reliably and consistently in terms of an initial 'lag' time followed by a $t^{1/2}$ power law dependence and a final curvature associated with 'gel' saturation.

When water enters the polymer, the overall crystallinity drops significantly, showing that the water is able to 'unzip' polymer–polymer intermolecular hydrogen bonds, allowing a gel to form. Thus PVOH does, in this case, allow water to 'enter' the crystalline domains.

The swollen 'gel' recovers at least part of the 'crystalline' organisation even though the kinetics become Fickian. The constant level of recovered 'structure' may be associated with an approximately constant ratio of acetone:water in the films at equilibrium (regardless of the ratio of concentrations in the reservoir).

At certain proportions of water to acetone in the solvent mixture, the two sorption curves are separated in time, implying that water needs to penetrate the polymer before acetone may enter the matrix. Whether the complexation of water with acetone is in any way responsible for such separation of sorption time scales is open to conjecture (and needs to be further explored).

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