*FT*i.r. study on the nature of water sorbed in poly(ethylene terephthalate) film*

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The interaction between moisture and poly(ethylene terephthalate) (PET) was investigated by *FT*i.r. spectroscopy over a near infrared range of wavenumber 4500–8000 cm^{-1} for an amorphous-isotropic film specimen as a function of relative humidity from dryness up to saturation at 30°C. From two water sensitive bands appearing at 5200 and 7000 cm^{-1}, the latter band (a combination of ν_{asOH} and ν_{sOH}) was mainly adopted to characterize the water sorbed in the specimen. To separate the water sensitive bands from the entire spectrum, two types of differential procedure were proposed: subtracting the spectrum at dryness from that at x% relative humidity (procedure A) and subtracting the spectrum at a given x% from that at $(x+\Delta x)$% relative humidity (procedure B), both as a function of x%. The moisture sorption isotherm determined from the area of the water sensitive bands thus separated by procedure A or B agreed well with that determined from a gravimetric method. The isotherm was found to follow a modified Henry's solution law. The 7000 cm^{-1} band was resolved into three sub-bands of Lorentzian type function centred at 6810, 7010 and 7090 cm^{-1}, which were compared with those of bulk water centred at 6715, 6887 and 7039 cm^{-1} in terms of three kinds of water species differing in the degree of hydrogen bonding. It is obvious that the three sub-bands of water sorbed in PET film shift to higher wavenumber than those of bulk water, but do not approach the spectrum of water vapour at $\approx$7200–7400 cm^{-1}. The relative humidity dependence of this blue shift was hardly found, with the exception of a slight increase of the shift at low relative humidities near dryness, leading to the conclusion that the water sorbed in PET is less interacted than in the liquid state and that few water species are strongly interacted with PET from dryness up to saturation.

(Keywords: moisture sorption isotherm; poly(ethylene terephthalate); sorbed water characterization; near infrared spectroscopy; 7000 cm^{-1} water sensitive band)

INTRODUCTION

Hydrophobic polymers usually absorb <1% water (g(g dry material)$^{-1}$) under saturation moisture conditions[1]. Nevertheless, the interaction of sorbed water with hydrophobic polymers has been a significant problem because even such a small amount of water affects considerably the physical properties of the materials, e.g. glass transition temperature, dielectric constant and Young's modulus. Poly(ethylene terephthalate) (PET) is included in this group of hydrophobic polymers. Recently, the effects of sorbed water on some physical properties of PET have been reported[2–5]. So far as the state and, consequently, the nature of the water sorbed in these hydrophobic polymers are concerned, very little information has been available due to difficulty in characterizing the intrinsically small water content.

Infrared spectroscopy is one of the outstanding techniques for characterizing the nature of the sorbed water in terms of relative absorbance and wavenumber of water sensitive bands, if detected. Recent progress in Fourier transform infrared (*FT*i.r.) spectroscopy has enabled us to detect and characterize the sorbed water in hydrophobic polymers, even though the amount of sorbed water is extremely small[6,7]. As has been pointed out by Luck[8], the overtone spectroscopy in a near infrared range is very useful for determining quantitatively the content as well as the degree of hydrogen bonding.

In a previous paper in this series of studies[9], the interaction of moisture with nylon 6 was investigated by *FT*i.r. spectroscopy over a near infrared range 4500–8000 cm^{-1}. Two water sensitive bands at around 5100 and 6900 cm^{-1}, combination bands of δ_{OH} with ν_{asOH} and of ν_{asOH} with ν_{sOH}, were adopted. The separation of these water sensitive bands from the entire spectrum was performed successfully by subtracting the spectrum of the dried specimen from that of the moisture conditioned one. The 6900 cm^{-1} band thus separated for the sorbed water and that of bulk water were resolved into three components for comparison with each other. The three components were attributed to three kinds of water species differing in the degree of hydrogen bonding, from single to doubly hydrogen-bonded water (ice-like water) species. From red shifts of the sorbed water components with respect to the corresponding bulk water components and their humidity dependences, it was concluded that the water species which interacted more strongly with each other also interact more strongly with the water accessible sites in nylon 6 to form a smaller number of adsorption layers in the sense of B.E.T.'s multilayer adsorption[10] or a core portion of water cluster in the sense of Hill's multimolecular adsorption[11].

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Spectroscopy in the near infrared range rather than in the mid-infrared range, has the following two advantages. First, it is possible to use an extremely thick specimen, up to 2 mm, which is slow enough in the change in moisture regain during *FTi.r.* measurements, even without any sealing of the specimen against the atmosphere[9]. Second, the assignments of water sensitive bands in the liquid state are more well established for the near infrared range than for the mid-infrared range[8,12–15].

In the study described here, the nature of the sorbed water in PET was investigated by *FTi.r.* spectroscopy in the near infrared range to characterize the sorbed water in comparison with that in the liquid or vapour state. Quite a contrast was deduced to the water sorbed in hydrophilic polymer of nylon 6.

TEST SPECIMEN AND EXPERIMENTAL PROCEDURES

Poly(ethylene terephthalate), with intrinsic viscosity of 0.685 in *p*-chlorophenol at 35.0°C, was extruded at ≈300°C by using a T-die device and quenched into warm water to form an isotropic (non-oriented) and amorphous original film 0.76 mm thick. The original film was cut into test specimens 50 mm long and 25 mm wide. The specimens were dried in a vacuum oven for 4 days at 50°C to prepare bone dry specimens. Under these conditions, the crystallization was believed to be negligibly small, if any, as revealed in *Figure 1* by the X-ray diffraction pattern. The bulk density of the specimen was determined by a density-gradient column method using a mixture of n-heptane with CCl_4 at 25.0 ± 0.1°C and is listed in *Table 1*. The degree of crystallinity X was calculated, as a weight fraction, from the bulk density ρ from the following two-phase equation:

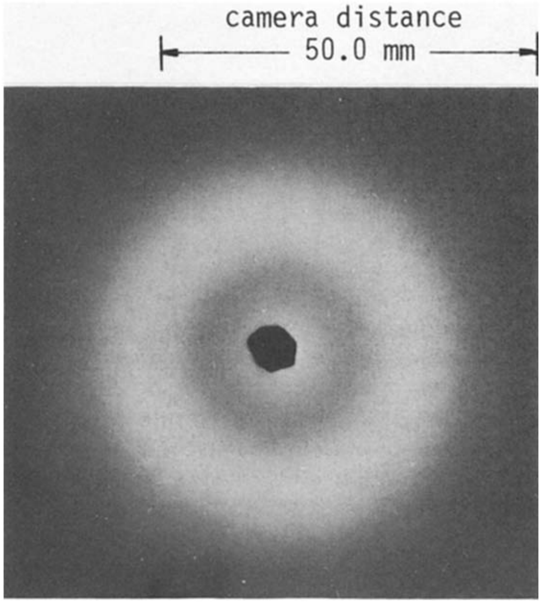

Figure 1 X-ray diffraction pattern of PET film specimen obtained by a flat film camera with camera distance of 50.0 mm

$$1/\rho = (1/\rho_{cry})X + (1/\rho_{am})(1 - X) \tag{1}$$

where ρ_{cry} and ρ_{am} are crystalline and amorphous densities, which were taken as 1.455 and 1.335 g cm^{-3} from the literature[16]. The density crystallinity X_ρ thus calculated was 3.3%, as listed in *Table 1*.

The moisture sorption isotherm was measured at 30°C by two types of gravimetric method: a weighing bottle method and a sorption balance method. In practice, a weighing bottle containing about 8 g of the bone dry specimen was kept in a desiccator to moisten the specimen at a given temperature and a given vapour pressure adjusted by an aqueous solution of sulphuric acid at a given concentration. Usually it takes as long as two weeks before an equilibrium of moisture sorption is achieved. In the present study, a set of 12 desiccators, with different concentrations of sulphuric acid covering the whole range of vapour pressure up to saturation, was stored in a huge air-bath thermostated by forced air-flow at 30°C.

The rate of moisture sorption or desorption was investigated by a sorption balance equipped with an electronic microbalance (Type GAB-1, Chyo Balance Manufacturing Co., Kyoto), also at 30°C, which the moisture up-take could be detected to the order of 1 μg. A typical sorption/desorption cycle of the specimen at a given vapour pressure of 15.2 mmHg* (47.8% relative humidity) is shown in *Figure 2*. An apparent diffusion constant for the sorption process can be evaluated from the initial slope of the sorption rate curve by the following well known Fickian equation:

$$M(t)/M(\infty) = 4(D_0 t/\pi l^2)^{-1/2} \tag{2}$$

where $M(t)$ and $M(\infty)$ are the mass uptakes at time t and at equilibrium, respectively, l is the thickness of the film specimen, and D_0 is the initial diffusion constant. The calculated diffusion constant was found to be 1.4×10^{-9} cm^2 s^{-1} for the sorption process, in fairly good agreement with a reported value of 3.9×10^{-9} cm^2 s^{-1} for a Mylar A film[17]. Moisture uptake at equilibrium in the sorption process was represented by percentage regain, defined as the moisture uptake per unit mass of the bone dry specimen. *Table 1* also lists the film thickness and the moisture regain at 65% relative humidity (r.h.) and saturation.

The infrared spectrum was measured by a transmission

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* 1 mmHg ≈ 133 Pa

Table 1 Physical characterization of poly(ethylene terephthalate) film at 30°C

Specification	Bulk density[a], ρ (g cm^{-3})	Degree of crystallinity[b], X_ρ (%)	Thickness (mm)	Moisture regain at 65% r.h. (%)	Moisture regain at saturation (%)
PET film quenched	1.3387	3.3	0.761	0.55	1.05

[a] Determined by density gradient column method with mixture of n-heptane/CCl_4 at 25.0 ± 0.1°C

[b] Determined as a weight fraction from the bulk density by using the following two-phase relation: $1/\rho = (1/\rho_{cry})X + (1/\rho_{am})(1 - X)$ and adopting the values $\rho_{cry} = 1.455$ and $\rho_{am} = 1.335$ (Reference 16)

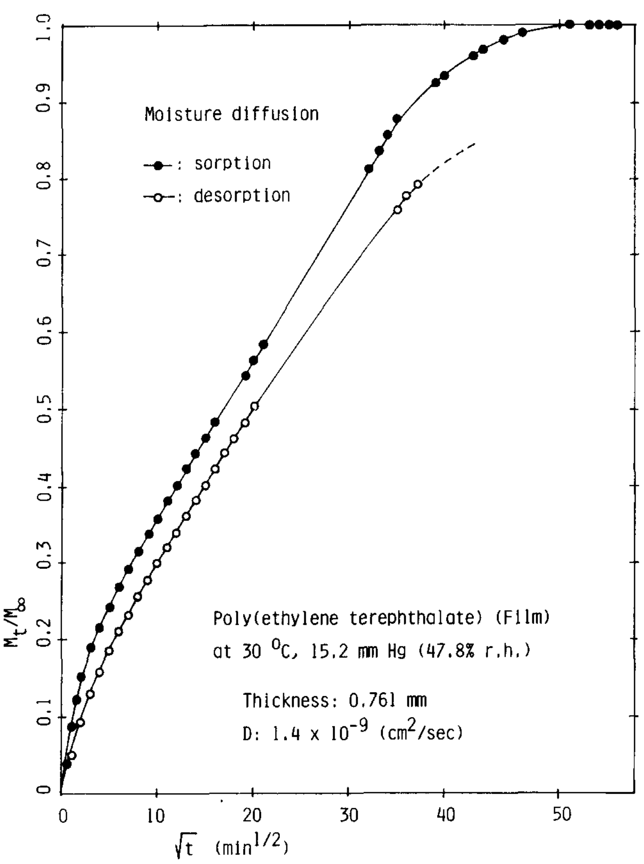

Figure 2 Moisture sorption/desorption rates of the PET film specimen observed by an electronic microbalance at 30°C and 15.2mmHg

technique using an *FT*i.r. spectrometer (Digilab Model FTS 15C) over a near infrared range 4500–8000 cm^{-1} on the PET specimens conditioned at various relative humidities at 30°C. A film specimen $\approx$2.3 mm thick (in practice a pile of the three conditioned specimens) was furnished for the *FT*i.r. measurement under a flow of N_2 gas. As recognized from *Figure 2*, the moisture sorption or desorption rate is slow enough to prevent any significant change in moisture content of the specimen during the *FT*i.r. measurement with more than 100 times scans. In fact, sealing of the specimen against the atmosphere was not needed to obtain reproducible results.

RESULTS AND DISCUSSION

FTi.r. spectra of conditioned specimens

Figure 3 shows the change in the near infrared spectrum of the bone dry specimen with the relative humidity at which the specimen has been conditioned at 30°C. Two water sensitive bands centred around 5200 and 7000 cm^{-1} are found to grow with increasing relative humidity.

To separate the water sensitive bands from the entire spectrum, two types of differential procedure were performed: the first overtone of the C–H stretching modes, a doublet at 5800 cm^{-1} (ν_{sCH} and ν_{asCH}), was taken as the internal standard to normalize the entire spectrum; and then the spectrum at 0% relative humidity (r.h.) was subtracted from that at x% r.h. (procedure A) or the spectrum at x% r.h. was subtracted from that at $(x+\Delta x)$% r.h. (procedure B), both for various values of x.

Figure 4 shows a series of differential spectra obtained by procedure A from the original spectra in *Figure 3*. The near infrared spectrum of bulk water is added as a reference. The separation of the two water sensitive bands from the entire spectrum seems to be satisfactory. The growth of the 5200 and 7000 cm^{-1} bands with sorption of moisture can be more clearly seen than in *Figure 3*.

From the area of the water sensitive bands thus separated, a moisture sorption isotherm can be composed, as plotted in *Figure 5*, on the assumption that the area is proportional to the concentration of the sorbed water. Although any correction due to the frequency dependence of the absorption coefficient[18] was not made, quite good agreement between the isotherm determined from gravimetry and isotherms determined by infrared spectroscopy can be achieved.

Analysis of moisture sorption isotherm

As shown in *Figure 5*, the sorption isotherm is nearly a straight line for low relative humidity and slightly convex to the abscissa for high relative humidity. The sorption isotherm of gas or organic vapour in glassy polymer has been described by a dual-mode sorption model in terms of Henry's solution law and Langmuir's adsorption[19,20]. If the concentration of Henry's law species dissolved in the matrix at standard temperature and pressure (s.t.p.) is C_D (cm^3(s.t.p.)(cm^3 polymer)$^{-1}$) and that of Langmuir species in holes is C_H (cm^3(s.t.p.)(cm^3 polymer)$^{-1}$), the isotherm can be represented by

$$C = C_D + C_H = K_D p + C'_H bp/(1+bp) \qquad (3)$$

where K_D is the Henry's law solubility coefficient (cm^3(s.t.p.)(cm^3 polymer)$^{-1}$ mmHg^{-1}), C'_H is the hole saturation constant for Langmuir adsorption (cm^3(s.t.p.)(cm^3 polymer)$^{-1}$), b is the affinity constant for a gas for the Langmuir sites ((mmHg)$^{-1}$) and p is the vapour pressure (mmHg).

Mauze and Stern[21] modified the dual-mode sorption model to describe the up-swing isotherm, rather than the straight line, in the high humidity region by assuming that C_D is a much stronger function of penetrant concentration or vapour pressure as follows:

$$C_D = [K_D \exp(\sigma C)]p \qquad (4)$$

where σ is a parameter characterizing the concentration dependence of C_D/p on the basis of the Flory–Huggins equation[22] and K_D can be determined from the initial slope of the isotherm at $p \approx 0$. Equation (3) for the dual-mode sorption model can be modified as

$$C = C_D + C_H = [K_D \exp(\sigma C)]p + C'_H bp/(1+bp) \qquad (5)$$

The observed sorption isotherm at 30°C in *Figure 5* seems to contain the C_D term, but not the C_H term (Langmuir's). The following values of K_D and σ reproduce the measured isotherm, as seen by the dashed line in *Figure 5*: $K_D = 0.375$ cm^3(s.t.p.)(cm^3 polymer)$^{-1}$ mmHg^{-1} or 0.715×10^{-2} % moisture regain/% relative humidity and $\sigma = 0.0204$ cm^3 polymer cm^{-3}(s.t.p.) or 33.9 as a reciprocal of percentage moisture regain. For CO_2 sorption in PET, it has been reported by Koros and Paul[23] that the dual-mode sorption model of equation (3) is applicable; the contribution of the Langmuir term decreases with increasing temperature and finally diminishes near the glass transition temperature. According to Jabarin and Lofgren[2] and Fuzek[3], the glass transition temperature of PET is reduced from 73°C at dryness to 58°C at saturation regain, which is, however,

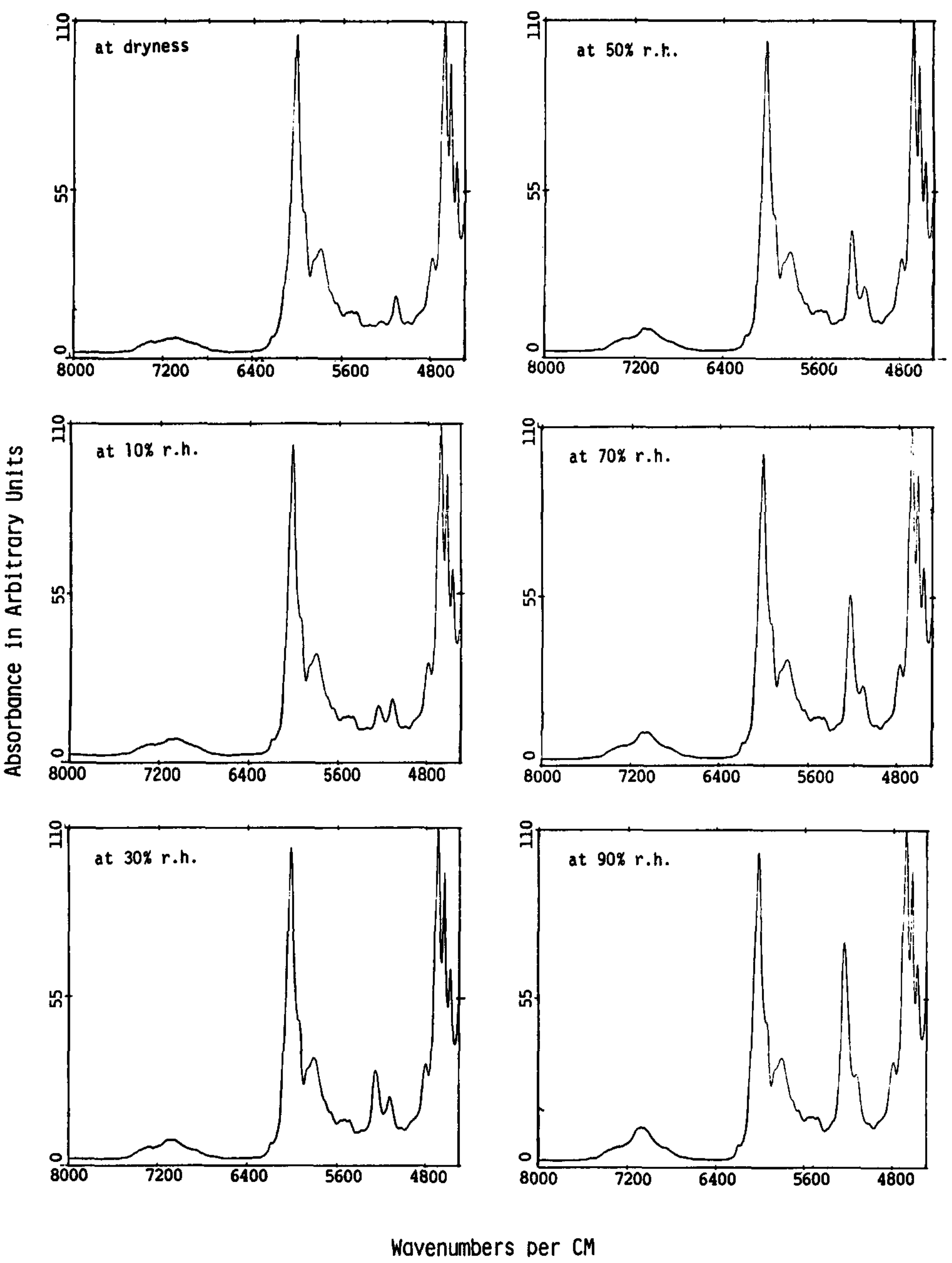

Figure 3 Change in near infrared spectrum of the PET film specimen over a range of wavenumbers 4500–8000 cm^{-1} for various relative humidities at 30°C

high enough compared with the present measuring temperature of 30°C.

Although the reason why the moisture sorption isotherm of PET at 30°C in the low humidity region can be described only by the Henry term without any contribution from the Langmuir term has not yet been clarified, it seems that there might be no 'hole' for adsorption sites in the sense of Langmuir monolayer adsorption. Several studies have reported the moisture sorption isotherm of PET to be represented by an almost linear function of vapour pressure and to be interpreted in terms of the Henry's dissolution law[2,17,24].

FTi.r. spectra of water in liquid and vapour states

It has been well established that water in the vapour state has three normal modes assigned to ν_{asOH}, ν_{sOH} and δ_{OH} centred at 3755, 3657 and 1595 cm^{-1}, respectively. In the liquid state, however, the spectrum becomes very broad and the assignments are still much disputed[15,25,26]. The O–H stretching region contains at least two broad bands centred at 3490 and 3280 cm^{-1}, while the O–H bending band is centred at 1654 cm^{-1}. That is, the O–H stretching bands are shifted considerably to lower wavenumber, while the O–H bending band is shifted to higher wavenumber than the corresponding wavenumbers in the vapour state.

Combination and overtone frequencies of water in the vapour state appearing in the near infrared range from 4500 to 8000 cm^{-1} are assigned as follows: a combination frequency of 5332 cm^{-1} as ($\nu_{asOH}+\delta_{OH}$); a combination frequency of 6874 cm^{-1} as ($2\nu_{asOH}+\delta_{OH}$); and a combination frequency of 7252 cm^{-1} as ($\nu_{sOH}+\nu_{asOH}$) (Reference 27).

As mentioned above, the O–H stretching modes shift

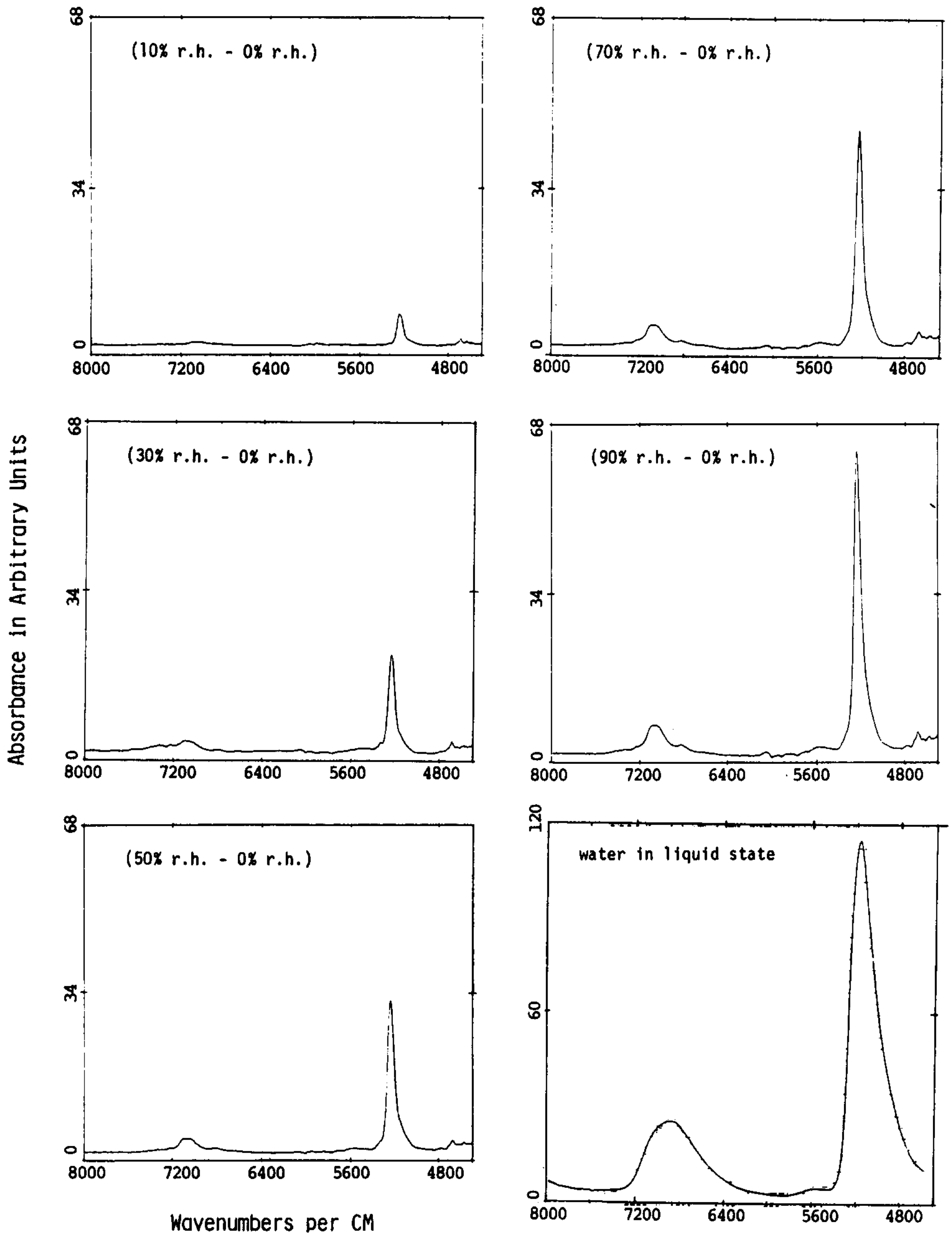

Figure 4 Change in the spectrum separated by differential procedure A with referenced relative humidity x%. The near infrared spectrum of bulk water is shown at bottom right for reference

to lower wavenumber, while the O–H bending mode shifts to higher wavenumber, both with increasing interaction between water molecules. This suggests that the 5200 cm^{-1} water sensitive band, which was observed for the moistened PETs and could be assigned to the combination of ν_{asOH} with δ_{OH}, is not suitable for discussion about the nature of the sorbed water from the frequency shift, and that the 7000 cm^{-1} water sensitive band, assigned to the combination of ν_{sOH} with ν_{asOH}, can be mostly used for further discussion on the characterization of the sorbed water.

Some examples of the 7000 cm^{-1} water sensitive band separated from the entire spectrum either by procedure A or by procedure B, are shown in *Figure 6* on an expanded wavenumber scale. Compared with the bottom right spectrum of liquid water in *Figure 4*, the shape of the 7000 cm^{-1} band of water sorbed in PET is not very different. The position of the band is shifted by about 100 cm^{-1}, as a whole, but not far enough to reach the wavenumbers of water in vapour state. To discuss in detail the nature of the water sorbed in PET, the differential spectrum of the 7000 cm^{-1} band is further resolved into three components of Lorentzian function by a method similar to that described in a previous paper[9].

Analysis of the water sensitive 7000 cm^{-1} band

The resolution of the 7000 cm^{-1} band into three components, sub-band I, I–II and II in the order of descending wavenumber, could be performed satisfactorily, as shown in *Figure 6* by dotted lines. At the top of the figure, the centred wavenumbers of the three sub-bands thus resolved are indicated by thick arrows at 7039, 6887 and 6715 cm^{-1}, respectively, for the water in the liquid state (bulk water). The spectrum of water in the vapour state was composed of many lines, among

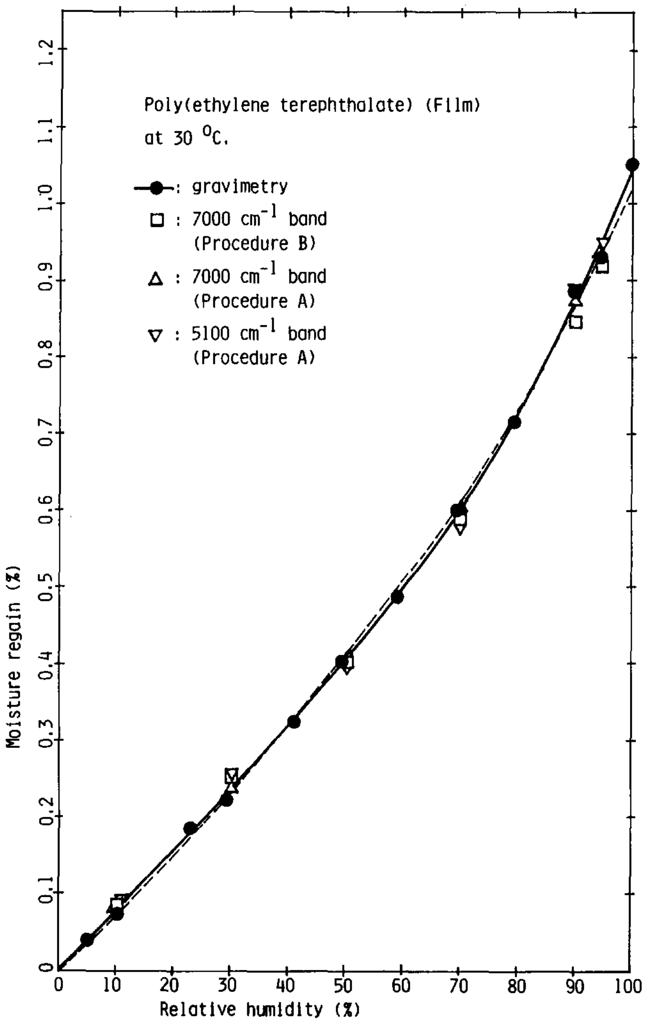

Figure 5 Comparison of the moisture sorption isotherm determined by a gravimetric method with those composed from the area of separated spectra of the 5100 and 7000 cm^{-1} water sensitive bands. ---, Line drawn according to equation (4) with the parameters indicated in the text

which the most intensive frequencies are indicated by thin arrows at 7340 and 7230 cm^{-1} in *Figure 6*. The final numerical results of the resolution are listed in *Table 2* in terms of the values of the Lorentzian function parameters. The three sub-bands for water in liquid state have been attributed to water species differing in the degree of hydrogen bonding, from singly to doubly hydrogen-bonded water (ice-like water) species[9].

Note that the corresponding three sub-bands for the water sorbed in PET are shifted to higher wavenumber by about 100 cm^{-1} than those of bulk water. That is, sub-band I of the sorbed water lies at a higher wavenumber than that of the bulk water, and sub-bands I–II and II of the sorbed water lie between sub-bands I and I–II and between sub-bands I–II and II of the bulk water, respectively. These blue shifts of the bands of sorbed water in PET relative to those of water in liquid state contrast with the red shifts of the bands of sorbed water in a hydrophilic polymer of nylon 6[9]. It is suggested that the water molecules sorbed in PET are much less interacted with each other, possibly with less degrees of hydrogen-bonding, than in liquid state.

Figure 7 shows plots of the centred wavenumbers of the three sub-bands determined by procedures A and B

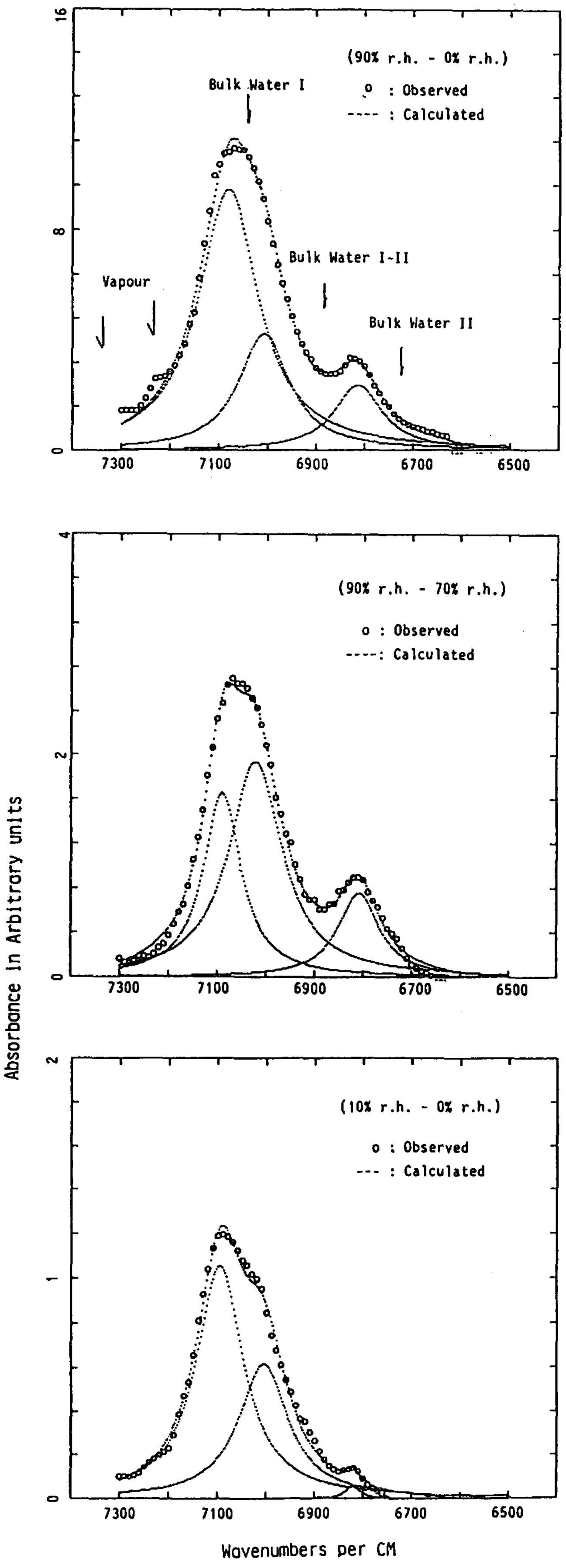

Figure 6 Some examples of the 7000 cm^{-1} water sensitive band separated by differential procedure A or B, and their resolution into three sub-bands. In the top figure, centred wavenumbers of the three sub-bands for bulk water and those of the two most intensive peaks for water vapour are indicated by thick and thin arrows, respectively

Table 2 Resolution of 7000 cm^{-1} band into three components of Lorentzian function

	Peak height (relative value)			Peak wavenumber (cm^{-1})			Half-width (cm^{-1})			Peak area (relative value)		
Specimen code	H_I	H_{I-II}	H_{II}	w_{0I}	w_{0I-II}	w_{0II}	W_I	W_{I-II}	W_{II}	$H_I \times W_I$	$H_{I-II} \times W_{I-II}$	$H_{II} \times W_{II}$
10% r.h.–0% r.h.	1.00	0.585	0.0553	7096	7006	6821	120	124	33.6	120	72.8	1.86
30% r.h.–0% r.h.	2.90	1.61	0.379	7103	7021	6801	133	106	41.3	385	171	15.6
50% r.h.–0% r.h.	4.27	1.11	0.926	7084	7012	6809	164	85.4	115	699	95.0	106
70% r.h.–0% r.h.	5.69	2.62	1.11	7087	7016	6809	146	118	95.2	833	309	105
90% r.h.–0% r.h.	7.84	3.53	1.69	7081	7007	6814	148	128	121	1160	447	205
95% r.h.–0% r.h.	8.57	2.65	1.92	7080	7007	6815	166	133	112	1420	352	214
Bulk water	1.00	1.42	0.945	7039	6887	6715	175	259	398			
10% r.h.–0% r.h.	1.00	0.585	0.0553	7096	7006	6821	120	124	33.6	120	72.8	1.86
30% r.h.–10% r.h.	1.64	0.338	0.425	7082	7009	6798	161	64.4	70.4	264	21.8	29.9
50% r.h.–30% r.h.	1.31	0.886	0.356	7086	7010	6821	101	124	70.8	132	110	25.2
70% r.h.–50% r.h.	1.26	1.55	0.207	7095	7019	6825	97.4	148	38.6	123	229	16.1
90% r.h.–70% r.h.	1.57	1.84	0.718	7090	7021	6809	93.9	133	103	148	244	73.7
95% r.h.–90% r.h.	–	–	–	–	–	–	–	–	–	–	–	–

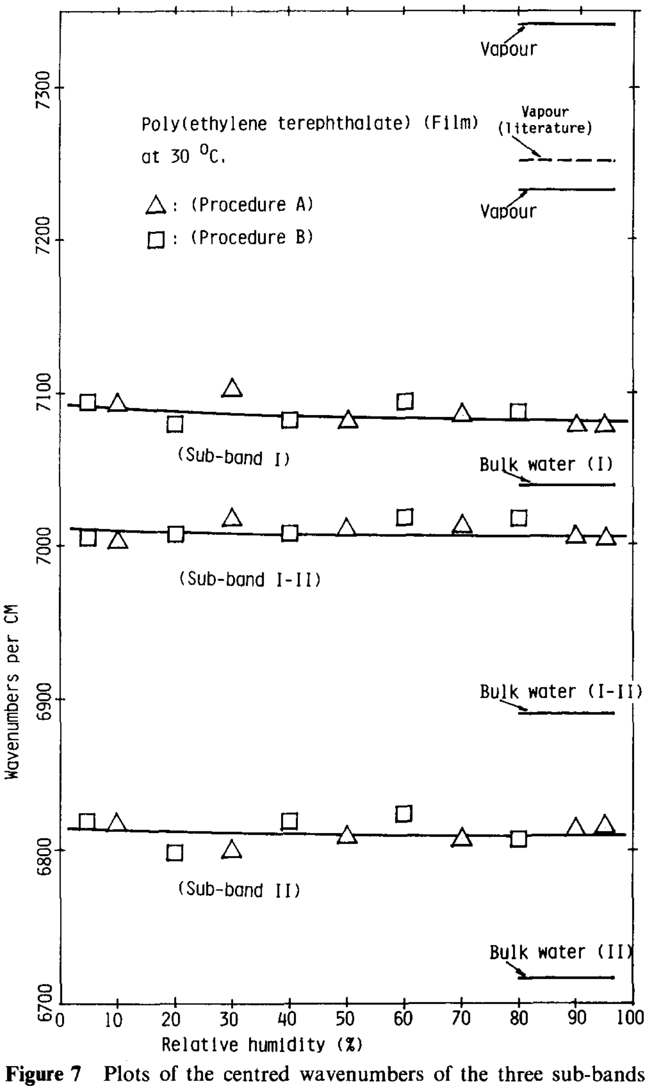

Figure 7 Plots of the centred wavenumbers of the three sub-bands against relative humidity. ——, Corresponding wavenumbers of bulk water and water vapour; ---, combination frequency of 7252 cm^{-1} (Reference 26)

for the sorbed water, all against the referenced relative humidity x%. The corresponding three centred wavenumbers of the bulk water and two wavenumbers of the most intensive lines for water vapour are indicated by thick horizontal lines. The blue shifts of each of the sub-bands of the sorbed water relative to those of bulk water, especially the relatively large blue shift of the sub-band I–II and the relatively small blue shift of sub-band I of the sorbed water, are obvious. The centred wavenumbers are slightly dependent on the relative humidity, i.e. the blue shift increases slightly with decreasing the relative humidity. This behaviour contrasts with that of nylon 6, for which the dependence was the opposite and more obvious: the red shift increased considerably with decreasing relative humidity. It can be concluded that the sorbed water species in PET interact less with each other than in the liquid state over the whole range of relative humidity, whereas the species in nylon 6, which interact more strongly with each other than in the liquid state, also interact more strongly with the water accessible sites with decreasing relative humidity.

On the assumption that the area of the resolved sub-band is proportional to the amount of corresponding water species, the relative amount of the water species can be plotted in the moisture sorption isotherm, as shown in *Figure 8*, where the dashed line was drawn by using the Henry solution law with $K_D = 0.715 \times 10^{-2}$ (moisture regain/relative humidity). The fractional ratios of the water species of sub-bands I, I–II and II are found to be roughly 60:30:10% at any relative humidity, whereas those of the bulk water are estimated to be 20:40:40%[9]. Taking into account the blue shifts of the respective sub-bands in *Figure 7*, considerable skew in the distribution of the degree of hydrogen bonding toward less interaction may be expected for the sorbed water in PET, i.e. the distribution may be mostly weighted with a degree of hydrogen bonding less than single for the sorbed water in PET and between single and double for the bulk water.

Henry's law may interpret the sorbed water to be randomly dissolved without any strong interaction with polymer chains. It is interesting to note that the isotherm of Henry's law drawn with $K_D = 0.715 \times 10^{-2}$ contains, at least, all of sub-band I. The water species of sub-band I must be far less ordered than in the liquid state, as clearly seen by the magnitude of the blue shift to higher wavenumber. In the water–hydrophobic polymer system, what Henry's law does mean is an important question. From the present *FT*i.r. study, at least the following can be concluded: water species obeying Henry's law have a degree of hydrogen bonding less than single, but not so small as to be comparable with water in vapour state.

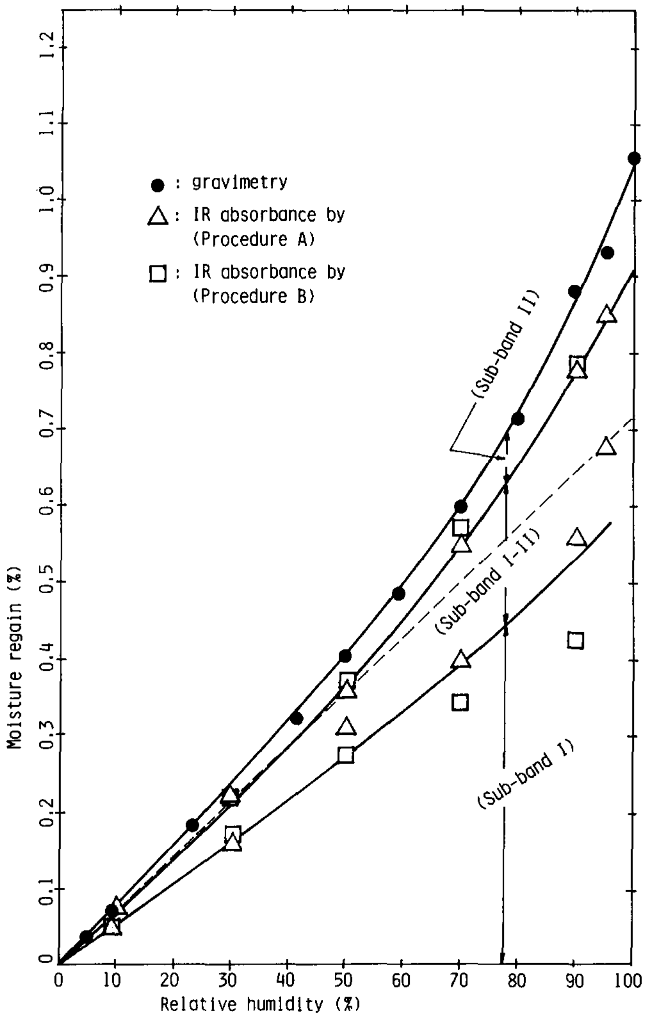

Figure 8 Resolution of the moisture sorption isotherm of PET film specimen at 30°C into three contributions from water species of sub-bands I, I-II and II. ---, Drawn by Henry's solution law with $K_D = 0.715 \times 10^{-2}$

Recently, Hatakeyama and Hatakeyama[4] have reported that there exists 0.5–1% non-freezing water in PET from a differential scanning calorimetric study, where non-freezing water means strongly bound water. The present *FT*i.r. study, however, indicates that there is no such strongly bound water in PET, unlike in nylon 6, in terms of the wavenumbers of the resolved sub-bands as well as of their almost absent relative humidity dependences. In fact, our calorimetric study has revealed that the wetting process of PET in water is primarily endothermic[28], as suggested in the present study. Although the values of 0.5–1% are unbelievably large from the viewpoint of the moisture sorption isotherm of PET in equilibrium, non-freezing water might correspond to the water species of sub-band II in this study.

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