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ORIGINAL CONTRIBUTION

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The structure of adsorbed water in cellulose acetate membranes

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Abstract The structure of water adsorbed in cellulose acetate membranes is determined by the fundamental and overtone IR spectra. Water is weakly H-bonded to ester and ether groups of the membrane, at low water contents. With increasing water content, more and more liquid-like water is observed. In addition, a small amount of a third type of water is present. The amounts of these three species are estimated from the spectra. At high water contents, the amount of liquid-like water increases strongly. The H-bond cooperativity of such water may be the cause for this increase and for the common anomalous water adsorption isotherms.

The H-bond energy of the first hydration shell is relatively small, contrary to the anomalous large adsorption heats ΔH_{ad}. This could be described by larger van der Waals interactions between this type of water and the membrane groups as a result of a higher coordination number compared with $Z = 4.4$ of liquid-like water. This model is in agreement with the decrease of ΔH_{ad} with increasing water sorption reaching the evaporization enthalpy of pure water at high water contents.

Key words Water – desorption – multilayer adsorption – water structure – water cooperativity – H-bonds – IR spectroscopy

Introduction

Recently, we published [1] isotherms of water desorption from three different cellulose acetate membranes. More than three different types of adsorbed water were indicated:

1. At low relative humidity p/p_0 (relative humidity) the water molecules interact with the membrane groups (hydrate water).
2. At higher relative humidity additional water appears to be more liquid-like.
3. Deviations from the BET theory with a two energy adsorption process indicated more than two different processes [1].

In addition, we observed [1] adsorption heats $\Delta H_{des} > \Delta H_{vap}$ (H_2O) at low relative humidity. ΔH_{des} decreases asymptotically with increasing water content till the evaporization heat of liquid water ΔH_{vap} (44 kJ mol^{-1} at 20 °C) is reached.

The aim of this paper is to recognize information on the different water species by IR spectroscopy. We found in earlier papers [2] smaller H-bond interaction energies ΔH_H between the adsorbed water and the cellulose acetate membranes than ΔH_{vap} (H_2O) in liquid water. This seems to be contrary to the large values of ΔH_{des}. We test these results with the same membranes. A similar anomalous type of water isotherms as on cellulose acetate were found on a large group of biochemical compounds [3]: collagen, gelatine, glucose, dextrane, polysaccharides, and starch [3, 4]. In these cases, we observed at $p/p_0 = 0.5$, a step in

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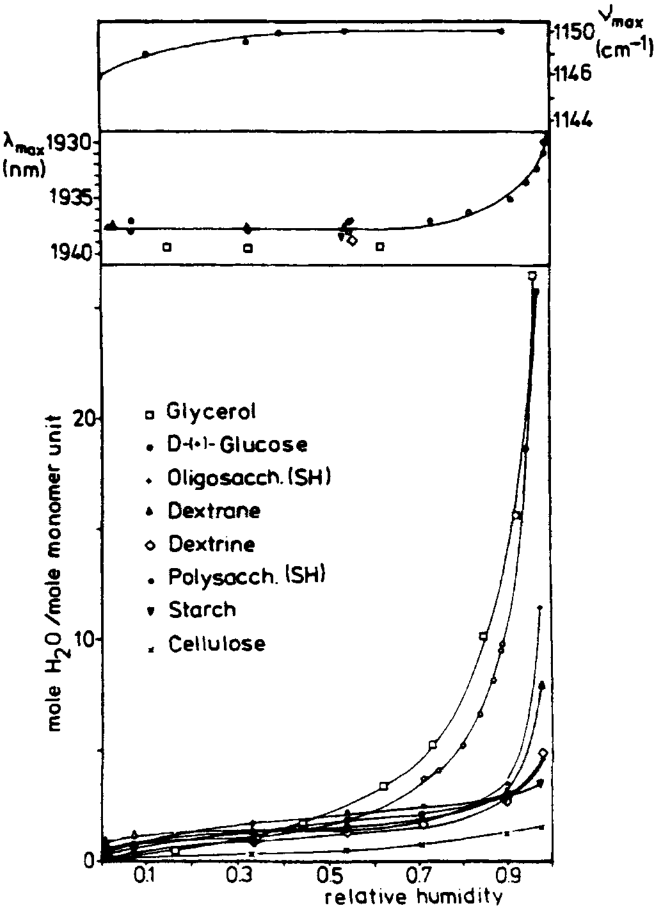


Fig. 1 Below: Desorption isotherms of different biopolymers [3]. Middle: band maxima of the water IR combination band. Top: IR band maxima of oligosaccharide

the water uptake corresponding to 1–2 mol water per mole monomer unit and, for larger water pressure, a strongly increase of water content up to 25 mol water per unit [3, 4] (Fig. 1).

Figure 1 shows typical examples of anomalous water take-up in biopolymers (unpublished data from earlier results [3]). Similar anomalous water adsorption isotherms are found in frog muscles or in egg albumin or in silk and nylon [5].

We found that the IR combination band (OH-valence plus bending vibrations) is a window to study IR OH-bands of water. This band is not influenced by alcoholic OH that occur in biochemicals [3, 4]. The reason is that the bending vibrations of H_2O and CH_3OH are different. For low relative humidities we found a frequency constancy of the water bands in collagen (in Fig. 1 in the middle). We correlated such bands with stronger H-bonds than liquid water ($\lambda = 1930$ nm) and considered the water as a first layer of hydrate water. We observed an increase of the band maxima frequency ν till the value of liquid water (Fig. 1, middle) in the region of the strong increase of the water content after saturation of this hydrate layer [3–5]. The H-bonds of the hydrate layer of humid collagen and hyaluronate are stronger than in liquid water [4]. The water isotherms of heparin show a hydrate at low relative humidity with weaker H-bonds than liquid water [4]. The isotherms of water sorption by chontroitin sulfate also indicate two types of water. The first hydration layer has similar strong H-bonds like liquid water [4]. Figure 1 (top) shows the shifts of the maximum of a band for an oligosaccharide, indicating a change of the biopolymer structure during the water-swelling process. In addition, a third type of water with a structure between the hydrate and liquid-like water could be observed [4]. It is interesting to know if cellulose acetate shows the same or different behavior and to uncover the reason for such a general anomalous water isotherms.

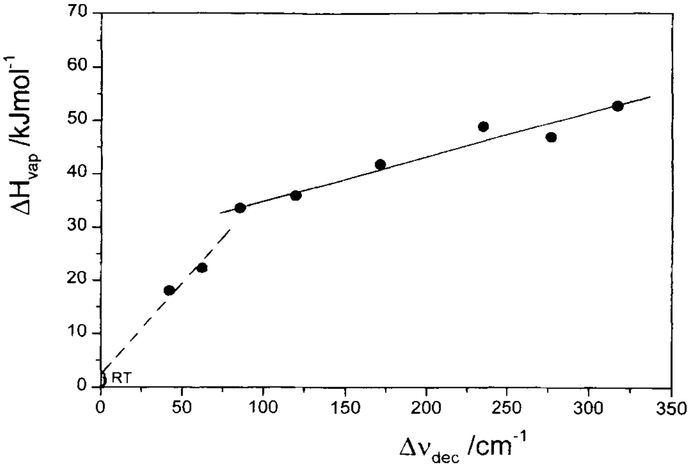


Fig. 2 The Badger–Bauer rule: linear dependence of the band maxima of the decoupled IR water fundamental band $(\nu_1 + \nu_3)/2$ as a function of the water evaporization heat of the infinitely diluted solutions (25 °C). From left to right: CCl_4, benzene, nitromethane, acetonitrile, tetrahydrofurane, dimethylsulfoxide, pyridine, triethylamine

The maxima of the vibration bands were determined. The so-called Badger–Bauer rule [7] for OH or NH valence bands expresses proportionality of the frequency shift $\Delta\nu = \nu(XH...B) - \nu$ (XH, vapor) and the heat of the H-bond energy ΔH_H [8–11]. We found [12] a similar but smaller $\Delta\nu$ by van der Waals interactions $\Delta H_{vdWaals}$ with $\Delta\nu$ of the overtone band of ethanol and water:

$$\Delta\nu = a\Delta H_H + b\Delta H_{vdWaals} + c \ . \tag{1}$$

We plotted $\Delta\nu$ as a function of the heat of vaporization ΔH_{vap} (water) from different solvents at infinite dilution in different solvents. In Fig. 2 the observed $\Delta\nu$ (water) is plotted as a function of ΔH_{vap} from different solvents extrapolated to infinite small water concentration. We observed $a > b$. Equation (1) allows an estimation of the van der Waals interactions [13, 14]. Equation (1) demonstrates that the IR $\Delta\nu$ is more sensitive to H-bonds than to van der Waals interactions. Probably, because $\Delta\nu$ is proportional to the gradient of the intermolecular potential. The gradients are proportional to the potentials for homologue systems.

On the other hand, we observed a remarkable polarization of the OH groups by H-bonds [14, 15]. $\Delta\nu$ (OH...base) is enlarged 30% by polarization of the OH by a second H-bond (OH...OH...B) [13]. H-bonded trimers, tetramers and so on are stronger and stronger, as the matrix spectra [16] and a theory show [17]. If we compare $\Delta\nu$ of a methanol dimer with $\Delta\nu$ of the long chains of H-bonds in liquid methanol, we observe $\Delta\nu$ (H-bonded polymer) = 2.3 $\Delta\nu$ (H-bond dimer) [18]. This means that polarization of three coupled H-bonds [14] is similar to the polarization of long chains of H-bonds in liquid alcohols [18]. In liquid water three groups of IR bands are correlated with non-H-bonded OH, weakly polarized H-bonded OH near the surface of water clusters and the strongly H-bonded OH in the center of water clusters. The strong polarized bands of multicoupled OH H-bonds in liquid water are similar 2.3 times stronger-shifted compared with the water H-bonds near the cluster surface [19].

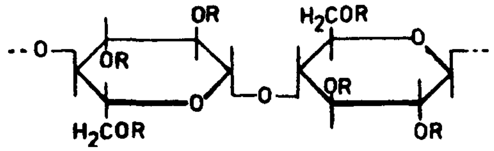
Figure 2 indicates that one single OH group of water forms an ether-like H-bond and multicoupled OH H-bonds as in dimethylsulfoxide or in ice-like triethylamine. We expect such strong shifts between the H-bonds of the second H_2O layer compared with liquid-like water.

Experimental

We used the same membranes with different contents of acetyl $-\overset{\overset{O}{\|}}{C}-CH_3$ as in Ref. [1] (Table 1) (All R=H in cellulose). We studied the absorption in the two infrared regions:

(i) The overtone region 4100–7600 cm^{-1}. In this field of absorption,
  (a) the overtone of H_2O $\nu_{13} = (\nu_1 + \nu_3)$, the sum of the fundamental symmetric valence vibration ν_1 and the asymmetric ν_3;
  (b) the so-called combination band $\nu_{23} = (\nu_2 + \nu_3)$, the sum of ν_3 and the so-called deformation vibration ν_2 and it is $\nu_{23} > \nu_{13}$.
(ii) The fundamental region 3000–4000 cm^{-1}.
  The region of the fundamental valence vibrations of water ν_1 and ν_3.

Table 1 Used disaccharide units



Membrane	E320	K700	T900
Molecular weight per unit	475	526	568
Numbers of $R=-\underset{\underset{O}{\|}}{C}-CH_3$ per unit	3.6	4.8	5.8
Numbers of R=H per unit	2.4	1.2	0.2
Thickness [μm]	140–144	140–144	100–104

For (i) we used a Cary photometer 17i with a thermostated cell compartment and a OS quartz cuvette [6] with an inflected glass container to deposit different aqueous salt systems for an adjustment of the equilibrium water pressure between $p/p_0 = 0.11$ and 0.95. The same salts have been used as in Ref. [1]. The thickness of this cell is 1 cm. A valve allows evacuation of the cell. The membranes have been fixed in the cell by a metal frame. The membrane thicknesses were appropriate for a convenient absorbance region of the fundamental vibrations of water. In the overtone region the water band intensities are smaller. Therefore, we observed overtone spectra with 1–5 membranes arranged parallelly. The cell has been filled with liquid CCl_4 to prevent interferences between different membranes. Because of the small solubility, the loss of water in CCl_4 was spectroscopically determined to be less than 3%. This spectrum of water dissolved in CCl_4 has been subtracted from the water spectra of membranes immersed in CCl_4. When a water-membrane spectrum was measured, CCl_4 was removed and the next p/p_0 was adjusted by changing the salt solution.

We used a Perkin–Elmer PE 325 instrument to measure the fundamental vibrations. The cell for the Perkin–Elmer contained two AgBr windows, separated by a Teflon ring. The Teflon ring had a connection to a vacuum pump and to a vessel with saturated salt solutions for the adjustment of p/p_0. The whole equipment was fixed together by two metal frames and was mounted in a thermostated box.

All measurements were started at high humidity and continued to low p/p_0 with a computer connection. The spectra were recorded when the equilibrium state was reached. At the end of the experiments, the membranes were dried for 10 h at 100–120 °C and their spectra were registered.

The membrane water desorption isotherms are determined for 10°, 20°, 30° and 40 °C. The spectroscopic experiments have been done only at one $T = 25$ °C.

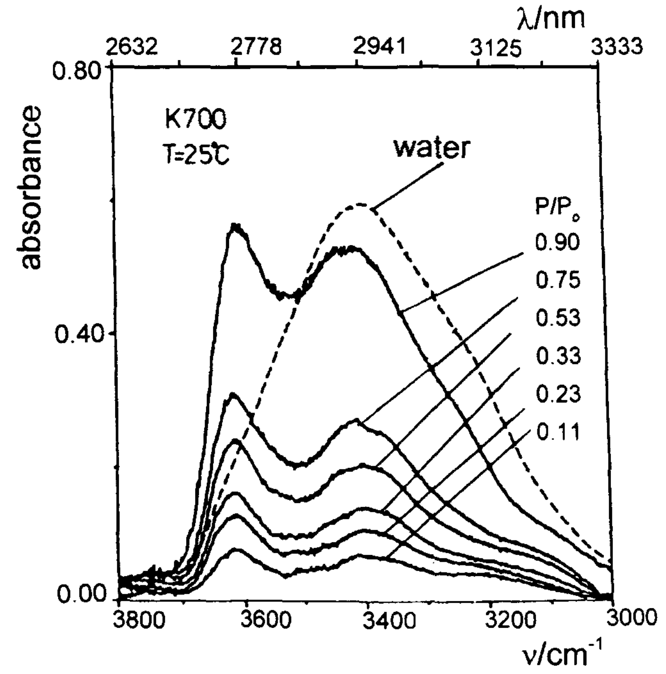


Fig. 3 IR fundamental band of water in K700 at different p/p_0 compared with liquid water. The spectrum of the dried membrane is subtracted

Results and discussion

The fundamental water band

The fundamental spectra of water have the following disadvantages: (1) the two broad OH vibrations ν_3 and ν_1 with a distance of about 100 cm^{-1} overlap and (2) they overlap with vibrations of the membrane OH groups. We can subtract this OH membrane band from the spectra of the water band [6]. But this subtraction (Fig. 3) is only an approximation because the membrane OH spectrum is also changed by adsorbed water. We observe two groups of bands: one with a maximum at 11% relative humidity at about 3614 cm^{-1} with a shoulder around 3550 cm^{-1} and a second around 3400 cm^{-1}; at 90% relative humidity, 3607 and 3422 cm^{-1} (Fig. 3, for K700). T900 gives similar spectra [6]. In this case we observe the following maxima at 11% relative humidity: $\nu = 3645$ and 3390 cm^{-1} and a shoulder at 3550 cm^{-1}; at 90% relative humidity: 3610 and 3445 cm^{-1}. The first band with broad maxima ν around 3607–3640 cm^{-1} is related to ν_1 and ν_3 of the following complexes in Table 2 [6] (the spectra of ester were determined for solutions of β-glucose-pentaacetate in CH_2Cl_2 [3]).

The differences of ν between 1 : 1 and 2 : 1 complexes on the left and right sides are induced by an anticooperativity polarization [20].

One H-bond with one OH group of water polarized the second OH "negative". This means the second H-bond of the second OH of one water molecule is weaker than the first H-bond of a 1 : 1 complex [20]. The last line in Table 2 is estimated for cooperative H-bonds to ester and ether groups.

The second maximum around 3400 cm^{-1} could be correlated with medium strong H-bonds of water molecules of about 2–3H_2O. A shoulder around 3390 cm^{-1} increases with increasing water content. This may indicate an increase of cooperativity by coupling of a larger number of water molecules. However, the fundamental spectra as in Fig. 3 give only qualitative indication because too many bands including the membrane OH band overlap in this region. Another difficulty is the fact that the intensity of the fundamental bands increases linearly with increasing $\Delta\nu$ (90% by a $\Delta\nu = 100$ cm^{-1}) or, respectively, with increasing interaction [21]. This is not the case for the overtone spectra [21, 22]. Overtone spectra of the water in membranes establish [6] the results derived from the fundamental spectra.

The combination band of water

The combination band of liquid water has a maximum around 5200 cm^{-1}, contrary to the OH combination of alcohols with the maximum smaller than 5000 cm^{-1}. In addition, only one water band ($\nu_3 + \nu_2$) dominates, contrary to the fundamental bands (ν_1 and ν_3).

Figure 4 gives the combination band of T900 in the presence of different water amounts. The dried membrane absorbs only in the region $\nu < 5050$ cm^{-1}. The maxima of

Table 2 Water IR frequencies in solutions with β-glucose-pentaacetate or diethylether in CCl_4

H–O–H...ester	3689 cm^{-1}	3552 cm^{-1}	Ester...H–O–H...ester	3637 cm^{-1}	3555 cm^{-1}
H–O–H...ether	3686 cm^{-1}	3500 cm^{-1}	Ether...H–O–H...ether	3590 cm^{-1}	3519 cm^{-1}
			Ester...H–O–H...O–H...ester	3615 cm^{-1}	3510 cm^{-1}
			H...ester	3637 cm^{-1}	3505 cm^{-1}
			Ether...H–O–H...O–H...ether	3650 cm^{-1}	3455 cm^{-1}
			H...ether	3590 cm^{-1}	3500 cm^{-1}

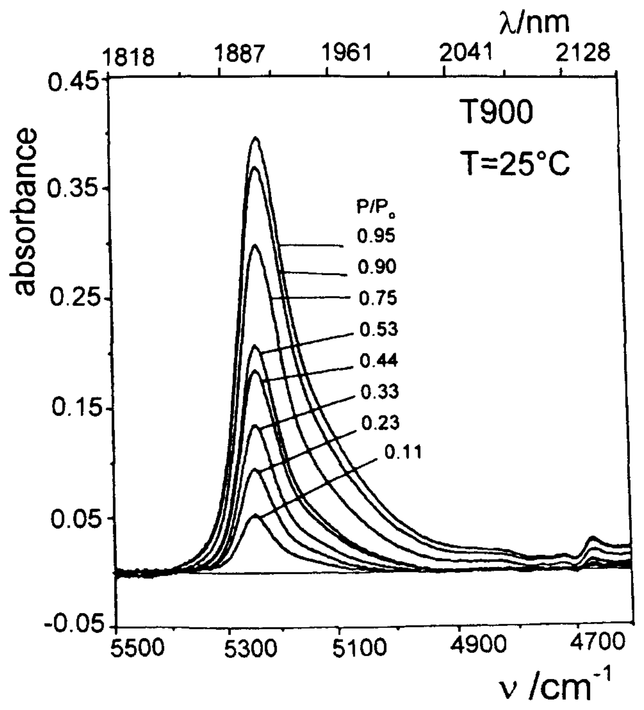


Fig. 4 IR combination band of water in membrane T900 at different p/p_0. The spectrum of the dried membrane is subtracted

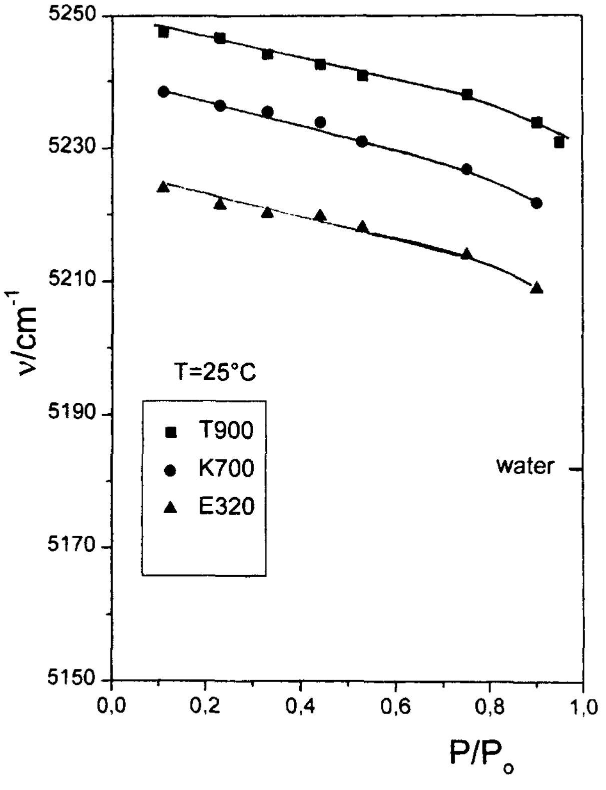


Fig. 5 Band maxima of the IR combination band of water in the three membranes as a function of p/p_0 compared with liquid water

the water band inside the membranes are observed [6] at:

rel. hum.	11%	95%
E320	5222 cm^{-1}	5210 cm^{-1}
K700	5237 cm^{-1}	5226 cm^{-1}
T900	5248 cm^{-1}	5235 cm^{-1}

The maxima are similar to the bands of water solutions in acetic/ethylester with 1 : 250 $\nu_{max} = 5225\ cm^{-1}$ and in diethylether with $\nu_{max} = 5220\ cm^{-1}$ [6]. The $\Delta\nu$ from T900 to E320 may be correlated with different ratios of ester to ether groups.

In dry membranes the ratio is:

	ester	ether	OH
T900	29	20	1
K700	4	3.3	1
E320	1.5	1.7	1

The band maxima shifts are given in Fig. 5 in dependence of the water content. $\Delta\nu$ shifts in the direction to liquid water. Comparing the water in the membranes, absorbances in the region 5200 to 5100 cm^{-1} increase from T900 to K700 and mostly in E320 parallel to the increasing water content in this series. $\Delta\nu$ is larger in the region $p/p_0 > 0.6$. The decrease of the ν-values (stronger H-bonds) could be caused by an increasing number of coupled water molecules which polarize the H-bonds more and more by interacting with ether or ester groups. On the other hand, this shift could be caused by an increasing overlapping with a band of liquid water with $\nu_{max} = 5182\ cm^{-1}$.

If we plot (Fig. 6) the absorbance coefficients (ε = absorbance/water content) for T900, we recognize that in the region of low interacting water (around 5260 cm^{-1}), the area decreases with increasing p/p_0 in a similar way as the area in the region of strong H-bonded water ($\nu < 5220\ cm^{-1}$) increases. It was observed in Ref. [3] that the combination band areas $\int \varepsilon\, d\nu$ of complexes of water with different bases with $45 < \Delta\nu/cm^{-1} < 200$ in CCl_4 as solvent increase (10% for $\Delta\nu = 155\ cm^{-1}$) only modestly with increasing $\Delta\nu$. This means in our case $\Delta\nu = \nu$ (ester) $- \nu$ (water) $= (5248 - 5182)\ cm^{-1} = 66\ cm^{-1}$ that we expect a band area increase of only 3–4%.

The nearly isosbestic cross section of all bands in Fig. 6 demonstrates that, in a first approximation, we could classify two types of water bands: with low and higher interaction energy. The water desorption isotherms demonstrate a stronger increasing of the absorbed water with increasing $p/p_0 > 0.4$; in this region $p/p_0 > 0.4$ $\Delta\nu$ changes more in Fig. 5. We observed [1] the following water uptake per monomer unit at $p/p_0 = 0.4$:

E320 : $2H_2O$, K700 : $1.6H_2O$, T900 : $1H_2O$.

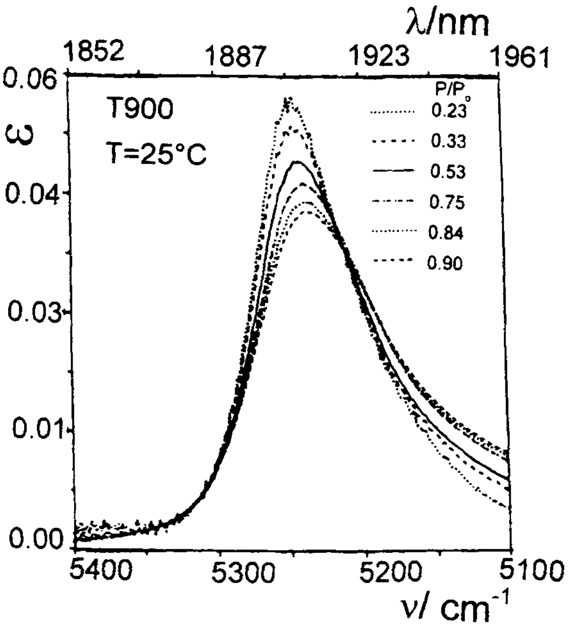


Fig. 6 Absorbance coefficient ε = water absorbance/water content in membrane T900

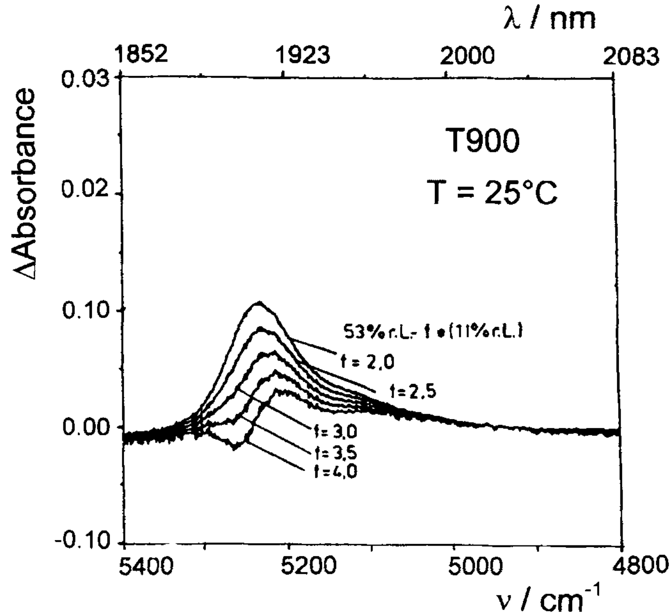


Fig. 7 Water combination band (in membrane T900) minus the hydrate band multiplied with a factor 1.5–4.0 (at $p/p_0 = 0.11$). The factor 2.5 gives the expected band profile

This small water amount and its parallel band positions near water...ester or ...ether complexes supports the assumption that this water is adsorbed as a monolayer hydrate at low p/p_0.

The half-width of the bands of Figs. 4 and 6 increase with p/p_0. This also indicates overlapping of two or more bands. From the difference spectra: water at a certain relative humidity minus the band of water absorbed at the lowest $p/p_0 = 0.11$, we can estimate the percentage of the type of water by calculating $\int \varepsilon \, d\nu$ [6]. The percent of hydrate decreases and the other type (liquid-like) increases with increasing water content.

A better estimation of these amounts of different water species in the membrane is obtained in the following method: We assume that the water uptake at $p/p_0 = 0.11$ corresponds to the pure hydrate. For instance, the membrane T900 absorbs at $p/p_0 = 0.53$ and 20 °C 4.65 times more water [1] compared with $p/p_0 = 0.11$. If we subtract from the absorbance spectra at $p/p_0 = 0.53$ the spectra of $p/p_0 = 0.11$ multiplied by 4.65 we obtain a negative value for the area, which means that at $p/p_0 = 0.53$ a second type of water is present. The procedure is shown in Fig. 7 for five different factors. If we vary the multiplication factor (Fig. 7 for: 2; 2.5; 3; 3.5 and 4) we can derive the largest factor which gives a difference spectrum with a normal IR band profile. In this case a factor 2.5 is found. When we assume that, absorption of 1 g water/100 g dry membrane at $p/p_0 = 0.11$ is only hydrate water, we conclude that for $p/p_0 = 0.53$ the 4.65 g water/100 g membrane composed of 2.5×1 g hydrate water/100 g membrane and 2.15 g water of different type. – In a second step we try to estimate the content of this liquid-like water: The band of hydrate water (Fig. 4) at $p/p_0 = 0.11$ ends at $\nu < 5000 \text{ cm}^{-1}$. Therefore, we subtract the spectra of liquid water multiplied by different factors from the spectra of adsorbed water and find the smallest factor which produces the difference spectra with zero absorbance at $\nu = 4960 \text{ cm}^{-1}$ (Fig. 8) for T900 and different relative humidities. By comparison of the areas we obtain the proportion of liquid-like water. If we subtract from the spectra of fig. 8 the spectrum of the hydrate water, we know its proportion from the method of Fig. 7, we obtain the spectrum of a third type of water ("rest water", Fig. 9). Similar "rest water" spectra could be determined independently by subtracting the spectrum of the hydrate water from the band of the total absorbed water (like Fig. 7). In this case too, we get bands which differ from bands of pure liquid-like water. This rest water indicates a third type of absorbed water type which has the band maxima of about 5210–5190 cm^{-1} and a shoulder at about 5100–5050 cm^{-1} (Fig. 9). The main maximum has a smaller wave number compared with the OH..ester or ...ether bands. This shifts may be caused by complexation with a short chain of water OH H-bonds and, therefore, a certain cooperativity exists. The observed shoulder has a larger $\Delta\nu$ too, compared with liquid water with $\nu_{max} = 5182 \text{ cm}^{-1}$. One possibility of these larger $\Delta\nu$ or

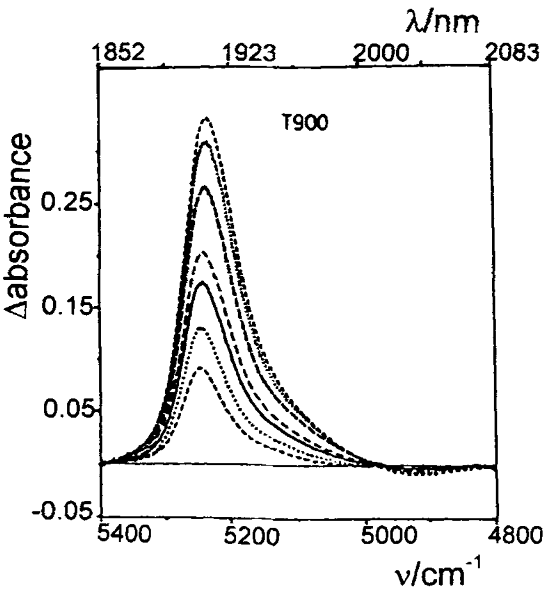


Fig. 8 Water combination band (in membrane T900) at different p/p_0 minus multiplies of the band of liquid water until the absorbance at 4960 cm^{-1} is zero as in the spectra of hydrates

stronger H-bonds could be caused by the so-called anticooperativity decrease in unsymmetric HOH complexes [20]. The 2:1 complexes B...HOD...B induce a smaller $\Delta\nu$ (25% weaker H-bond) compared with the H-bond in 1:1 complexes, because the H-bond with one B polarizes the neighboring OH group negative to reduce the H-bonding ability. The anticooperativity in an asymmetric 2:1 complex B′...HOD...B with a weaker base B′ (weaker than B) is smaller than in a symmetric 2:1 complex with two stronger bases B. In our case, the direct asymmetric H-bonded water of the hydrate layer to the water ester/ether ...HOH...OH has a weaker cooperativity polarization by the membrane group or a stronger H-bond donor ability on OH of the hydrate than a water in the pure liquid. Such hydrate groups could induce stronger water...water H-bonds. Thus, the second water layer has different H-bonds compared with the third water layer.

We can determine the proportions of these three bands by comparing the areas of these three bands. If we multiply now the total water amount determined in Ref. [1] at every p/p_0 with these spectroscopically determined percentages, we obtain Fig. 10. Figure 10 provides a possibility to describe the anomalous water isotherms for the total water:

1. The hydrate forms. We know from the adsorption of small amounts of simple solvents that water or alcohols enter the membranes by a swelling mechanism.
2. Parallel to the swelling of these membranes liquid-like water is adsorbed with increasing p/p_0. When such species are formed inside the membrane, then multilayers of water are created because the polarization of the H-bonds promote formations of additional water...water H-bonds. A condition is that the membranes can swell.
3. A third species of water increases with increasing hydration. Perhaps that additional membrane groups are engaged in the swelling mechanism. This agrees with the idea that this "rest water" represents the second water layer. Not all layers may be able to accept a second water.

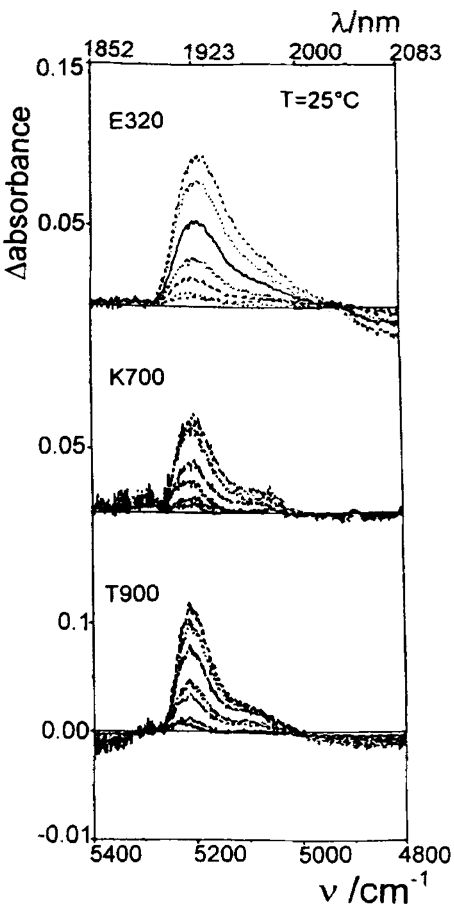


Fig. 9 Spectra of the third type of water in the membranes. These spectra are spectra of type as in Fig. 8 minus the spectra of the determned part of hydrate

Such "rest-water" was also observed for water/gelatine mixtures [4]. In this case the first hydrate water at low amounts is more strongly H-bonded liquid-like water. In the cellulose acetate membrane the water molecules are more weakly H-bonded.

The two main types of water were also observed by NMR technique in water/biopolymers [23]. Our study demonstrates that the anomalous isotherms with increasing amounts of liquid-like water at large water contents

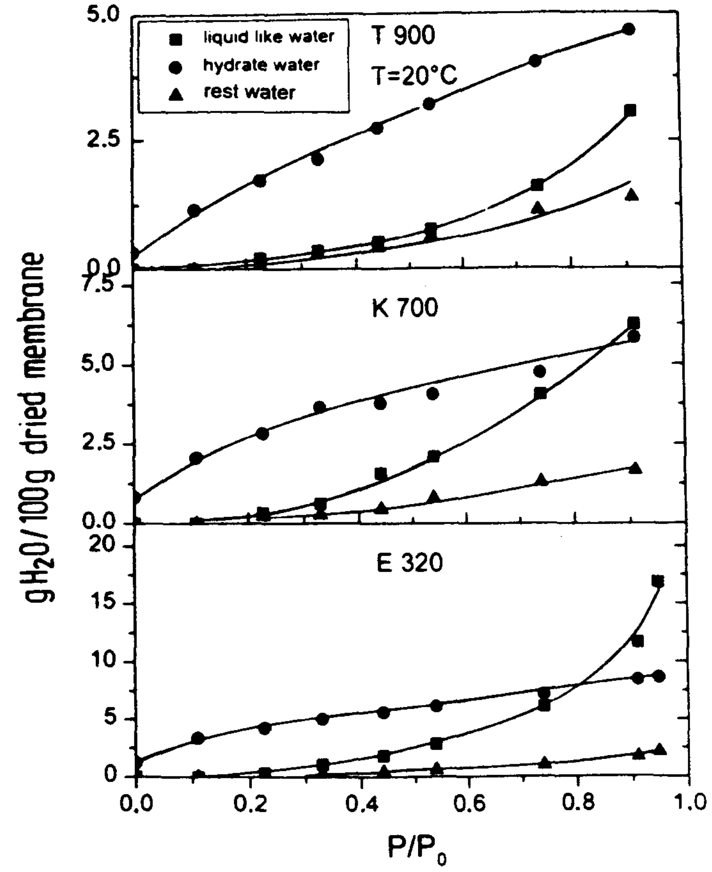


Fig. 10 Spectroscopic estimation of the proportions of water species type 1, 2 and 3 at different p/p_0

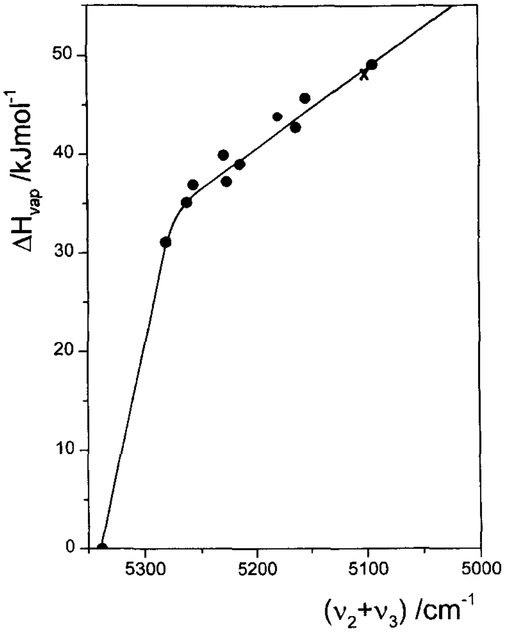


Fig. 11 The Badger–Bauer plot of the water combination band, determined with 2 : 1 complexes B...HOH...B of different bases B in CCl_4. Water-vapour: 5337 cm^{-1}, Bases (from left to right): CH_3NO_2; CH_3CN; $(CH_3)_2CO$; $C_2H_5COCH_3$; $(C_2H_5)_2O$; tetrahydrofurane; liquid water; C_2H_5OH; $(CH_3)_2SO$; x : ice

may be induced by the cooperativity. The H-bond strength is enhanced in multilayer water and promotes progressing swelling process. Parallel to this swelling, the intensity of the acetate membrane bands in the region 1000–1300 cm^{-1} increases at $p/p_0 > 0.53$ [6]. This indicates a change of the polymer structure. The increase of the water affinity at large p/p_0 may be caused by the H-bond cooperativity and give a key to understand the anomalous water isotherms in many cases [24].

The adsorption of liquid-like water is favored in E320 > K700 > T900 (Fig. 10). This series is parallel to the OH content of the membranes and also increases the ion rejection. Thus, increasing amounts of liquid-like water reduces the use of the membranes for desalination processes.

We showed in an earlier paper [25] that the ions (exception of K^+) increase the H-bond formation in liquid water. We concluded from the limited solubility of salts in water that every ion needs a cluster of surrounding water molecules [25]. Only the sum of this more ordered water is able to produce the fairly large heat of solubility of ions in water. The ion separation of the membrane is based on the inability to solve larger water clusters necessary for every ion. The strong-hydrated ions cannot pass the membranes. However, water flux can occur due to the lower H-bond energy of the hydrate, which needs a lower activation energy. The mobility of the hydrate water may require locally smaller energy contributions. Details of this mechanism can be studied in future.

The water-membrane interaction energies

A comparison of the band maxima of the fundamental band at low relative humidity with $\Delta(\nu_1 + \nu_3)/2 = 90\,\mathrm{cm}^{-1}$ of Fig. 1 establishes the low energy of water H-bonds in cellulose acetate. The observed $\Delta\nu$-values correspond to the water interacting with nitromethane or acetonitrile $\Delta H_{\mathrm{H}} = -34$ kJ/mol. On the one hand, it establishes our earlier spectroscopic results in Ref. [2]. On the other hand, this is in contrast to the desorption energy $\Delta H_{\mathrm{des}} = 60$ till 74 kJ/mol [1] or to results of Pusch and Burghoff [26].

We get a similar result with the more precise combination band $(\nu_2 + \nu_3)$. Figure 11 shows the Badger–Bauer plot of 2 : 1 water complexes B...HOH...B in CCl_4 with different bases. We observe $\nu_{max} = 5237\,cm^{-1}$ (K700) and $\nu_{max} = 5220\,cm^{-1}$ (E320) for water at $p/p_0 = 0.11$. Such band maxima correspond to ester solutions (fourth point from left Fig. 11) with $\Delta H = -37$ kJ/mol. These ΔH values are much smaller than the adsorption energies [1, 26]: ΔH_{des} (E320) = 72 kJ/mol and ΔH_{des} (K700) = 67 kJ/mol. As discussed in Ref. [1], these differences could be understood by assuming larger van der Waals interactions of water in membranes by larger coordination numbers of the hydrate water compared than 4.4 in liquid water. The positions of IR bands are dominated by the H-bond interactions. Van der Waals interactions are only second-order disturbations in IR spectra [13, 14].

There is one possibility to combine all these results. The van der Waals forces for the hydrate could be larger than in simple normal liquids. This supposition agrees with the spectroscopic observations [27] that, in homologue series, the van der Waals forces change parallel with the density (ρ (methylacetate) = 0.934 $g\,cm^{-3}$; ρ (cellulose acetate) = 1.3 $g\,cm^{-3}$ [1, 28]). Figures 2 and 11 show that the van der Waals energies of simple liquids induce only small $\Delta\nu$. We can conclude from our experiments that IR experiments overstress the H-bonds. IR spectroscopy is a good method to study H-bonds. However, the van der Waals interactions have also to be considered.

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