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ORIGINAL CONTRIBUTION

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Water desorption isotherms of cellulose-acetate membranes

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Abstract The water desorption isotherms are determined in three cellulose acetate membranes with different acetyl content as a function of p/p_0 at 10–40 °C. The partition coefficients (adsorbed water over water pressure) show a minimum at $p/p_0 = 0.5$–0.6. This indicates a two energy mechanism. The agreement of our results with the BET adsorption isotherms only till $p/p_0 < 0.3$ shows that a two energy adsorption mechanism is valid only for small water contents, probably one hydrate layer and a second more liquid-like water layer. At large p/p_0, the adsorbed water becomes more and more liquid like by polarization of the hydrogen bonds. The heat of desorption is larger than the vaporization heat of water $\Delta H_{\text{vap}}(H_2O)$. It decreases with increasing water content asymptotically to $\Delta H_{\text{vap}}(H_2O)$. The cause may be a larger van der Waals interaction of the hydrate layer due to coordination numbers larger than 4.4 as in liquid water. Additionally, we found a hole adsorption process by sorbing unpolar solvents. The water and methonal adsorption are 100 times larger due to a swelling mechanism depending on the number of acetyl groups in the membranes. The amounts of n-alcohols sorbed decrease with their chain length.

Key words Membranes – water desorption – desorption heat – adsorption mechanism – multilayer adsorption – partition coefficients – water cooperativity

Introduction

Cellulose acetate membranes are a useful tool for water desalination processes [1, 2]. Some years ago, we determined by IR spectroscopy a H-bond interaction energy ΔH_H between adsorbed water and such membranes [3, 4] smaller than in liquid water. On the other hand, Burghoff and Pusch [5] observed larger heat of adsorption of water compared with the heat of vaporization of water ΔH_{vap}.

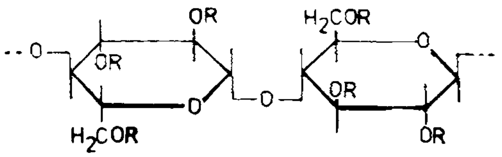
Therefore, we start to compare both methods, hoping to be able to clear up this apparant discrepancy.

Experimental [6]

We used the same cellulose acetate membranes of the Pusch lab. with different acetyl degrees. We received three different membranes by Dr. Wolfgang Pusch (Table 1).

The self-constructed equipment for adsorption measurements is shown in Fig. 1. We fixed a quartz spring of Fa. Heraeus at a double wall glass container. This container was thermostated by a flow of water of a thermostat Fa. Haake. The temperature T was measured by a Cr–alumel thermoelement and was constant within ± 0.1 °C between the spots 2 and 5. The length of the

Table 1 Disaccharide units



	E320	K700	T900
Molecular weight per unit	475	526	568
$R = -\overset{O}{\overset{\parallel}{C}}-CH_3$ per unit	3.6	4.8	5.8
R = H per unit	2.4	1.2	0.2
thickness/μm	140–144	140–144	100–104
(in cellulose all six R are H)	–	–	–

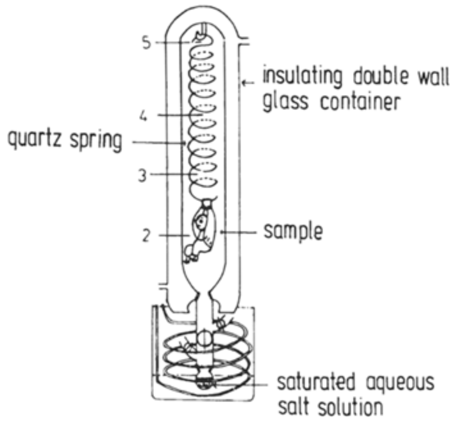


Fig. 1 Apparatus for desorption measurements by a quartz spring

quartz spring has been observed by a cathetometer to ± 0.01 mm and balanced by platinum weights of 10–200 mg. The spring length has been depending linearly on the weight. The length of the spring has been T-dependent but the temperature coefficient has been T-constant in the range of 10–40 °C. The volume of the balance could be evacuated by two small valves. Then, different relative humidites (of about 11%; 23%; 33%; 44%; 58%; 71%; 75%; 84%; 90%; and 95%;) could be attained by different saturated aqueous salt solutions of LiCl; CH_3COOK; $MgCl_26H_2O$; K_2CO_3; $MgNO_36H_2O$; NaBr; $SrCl_26H_2O$; NaCl; KCl; $BaCl_2$ and Na_2HPO_4, respectively. The relative humidity p/p_0 has been taken from literature [7–12] and T-extrapolated if necessary.

The membranes have been dried at 100–120 °C for about 10 h to evaporate rest of the solvents. In the next step these membranes have been saturated in liquid aqua bidestillata for two weeks. A piece of about 200 mg was attached at the spring, and measurements were started with the salt solution of the highest p/p_0. Before starting the measurements the balance container was evacuated to 0.5 Torr.

Desorption method

Normally, we started at the highest $T = 40\,°C$ and the salt solution of the highest p/p_0. Weight constancy required about 2 days. In the next step a salt solution with the next lower p/p_0 has been used and so on. At the end, the dry weight of the membranes has been determined by two methods:

I. The membranes have been heated in the evacuated balance container at 85 °C and its weight determined by the quartz spring.

II. The membrane has been taken from the balance and dried over P_4O_{10} for 24 h. After that, the membrane has been weighed at different times t and the weight has been extrapolated to $t = 0$.

The difference between the two methods of drying was not larger than 5%.

Results

Isotherms

Figures 2–4 show desorption measurements of the three different types of membranes. The water content in the polymers is given in gH_2O per 100 g dried polymer as a function of the relative humidity in the vapour phase at three different T. At the lowest T, the highest amounts are sorbed.

The amounts of water desorbed from membrane E320 are plotted in Fig. 5 as a function of the pressure p of water. The comparison of the three membranes (Fig. 6) reveals the sorption of water to increase with the content of OH groups in the polymer.

The data of Fig. 6 has been reproduced with a slightly different method. In this case the T-dependence at $40\,°C > T > 10\,°C$ has been measured with the procedure repeated. In this series we received similar results for all three polymers, but the values were about 10% smaller.

Two different affinities

The affinity of a compound between two different phases increases with the size of the partition coefficient. In our

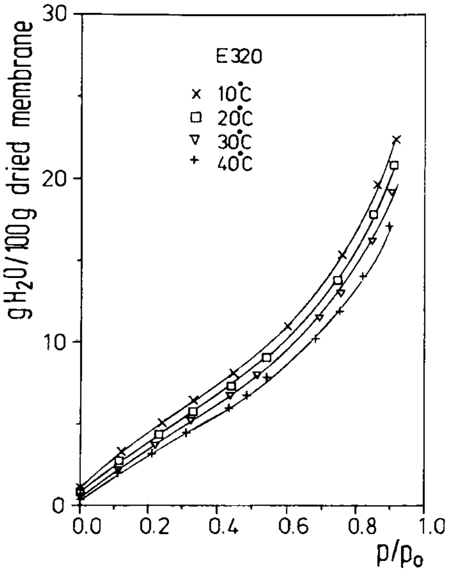


Fig. 2 Water desorption isotherms of E320 at different relative humidities p/p_0 at different temperatures. p_0: equilibrium vapour presure of pure water

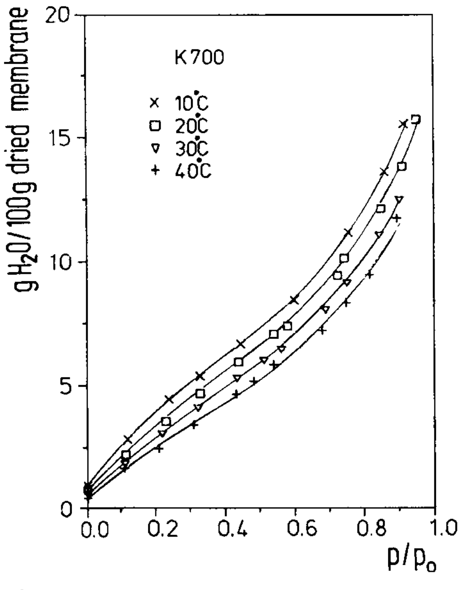


Fig. 3 Water desorption isotherms of K700

case, we could compare the water uptake (in gram) by 100 g of polymer divided by the water pressure p in the vapour phase. Such data are given by Figs. 7 and 8 and Fig. 17 in [6]. We recognize two different adsorption mechanism:

1. At low p/p_0 the affinity decreases with increasing p/p_0.

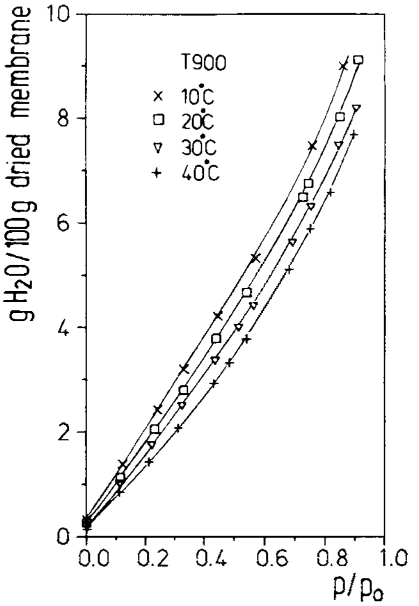


Fig. 4 Water desorption isotherms of T900

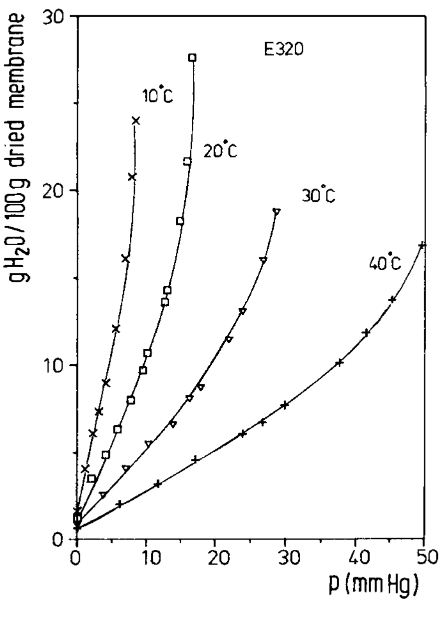


Fig. 5 Water desorption isotherms of Fig. 2 plotted as function of the vapour pressure p of the vapour phase

2. A minimum of affinity appears at certain p/p_0 values (see Table 2).

A comparison between Figs. 4 and 5 demonstrates that the representation as function of p/p_0 is correct corresponding to the related mechanism.

3. At higher p/p_0 the affinity increases with increasing p/p_0.

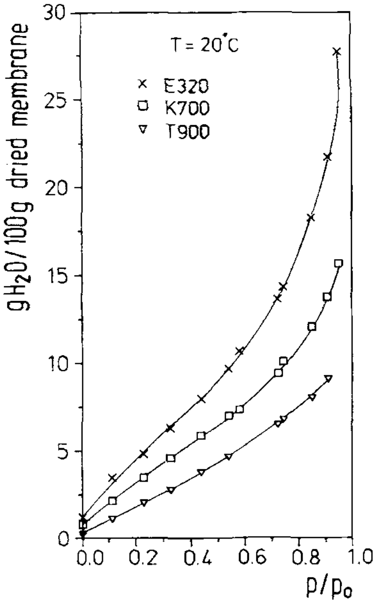


Fig. 6 Comparison of the desorption isotherms of Figs. 2–4 for the three different membranes at $T = 20\,^{\circ}\mathrm{C}$

Table 2 p/p_0 at the minima of the partition coefficients

	T [°C]	10	20	30	40
For E320		0.56	0.545	0.48	0.48
For K700		0.6	0.58	0.57	0.46
For T900		0.55	0.525	0.5	0.48

We assume that the first hydrate layer of water at the cellulose acetate differs from the second water layer and so on. We observed such a mechanism by spectroscopic studies of water sorption by tendon or gelatine [4, 13]. We could show experimentally [14] that intermolecular forces do not depend on the polarizability only. They polarize each other. This effect is especially strong in the case of H-bonds [14]. The H-bonds shift the charges. As a consequence the H-bond to a base increases in the series:

$$\mathrm{OH \ldots B < OH \ldots OH \ldots B < OH \ldots OH \ldots OH \ldots B.}$$

This cooperativity seems to be important for the anomalous water isotherms.

If we plot the ordinates of Figs. 7 and 8 as a function of the water content in the membrane ($w = \mathrm{gH_2O}/100\,\mathrm{g}$ dried membrane), we obtain the minimum which changes only slightly with T as in the last table.

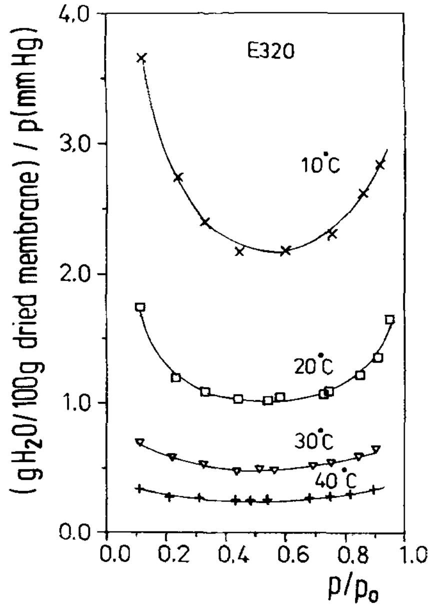


Fig. 7 Partition coefficient of water of E320: adsorbed water per 100 g membrane divided by the water pressure

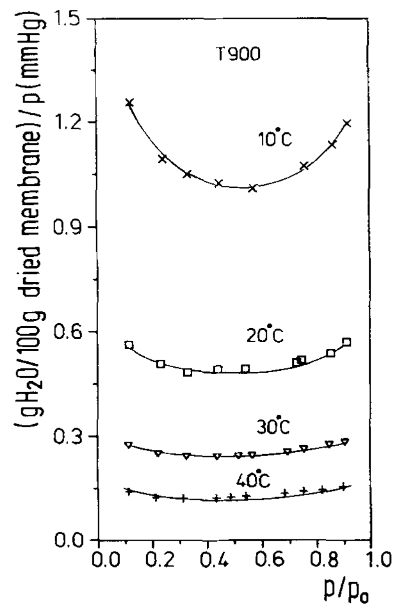


Fig. 8 The partition coefficient of water in T900

Temperature dependence

The heat of vaporization of a liquid ΔH_{vap} is determined by the T-dependence of its vapour pressure p_0:

$$\ln p_0 = \mathrm{const.} - \Delta H_{\mathrm{vap}}/(RT) \,. \tag{1}$$

For pure liquid water $\Delta H_{vap}(H_2O, 20\,°C) = 44$ kJ/mol. We obtain the desorption heat ΔH_{des} by an equation similar to Eq. (1), if we plot the water pressure which corresponds to a constant water content in the membrane as a function of $1/T$. We get really linear relations for our three different polymers. This is shown for three different water contents 2, 4 and 7 g per 100 g dry membrane in Fig. 9 for K700 and T900. Similar straight lines are obtained for E320 too [6]. The results of ΔH_{des} of our measurements are given in Fig. 10 as a function of the water content of the three different membranes. Indeed, we got larger values for $\Delta H_{des} > \Delta H_{vap}(H_2O)$. Figure 10 establishes the results of Burghoff and Pusch [5] and clarifies why, by IR spectroscopy [3, 4], smaller H-bond energies of water are found inside the membranes compared with liquid water.

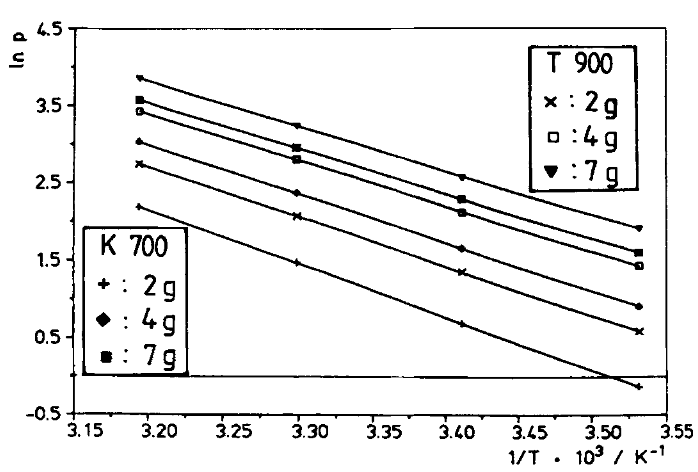


Fig. 9 Correlation between ln p at different constant water uptake (2.4 and 7 g H_2O/100 g dried membranes T900 and K700) and the reciprocal absolute temperature

ΔH_{des} decreases from relatively large values for E320 (about 30 kJ/mol larger than $\Delta H_{vap}(H_2O)$) and reaches asymptotically the values of pure water $\Delta H_{vap}(H_2O)$ at large water contents. At the minima of the water partition coefficients in the Figs. 7 and 8 and in [6] we observe the following water contents at 20 °C in g water/100 g membrane: E320 (9); K700 (7) and T900 (4.3). For these water contents of the different membranes ΔH_{des} equals about 50 kJ/mol (Fig. 10).

Solvent uptake of the membranes

We determined the uptake of organic solvents in our membranes. In this way, we hoped to arrive to a clearer knowledge of the water adsorption mechanism. For such experiments, the membranes have been dried by heating at 110 °C. The dried membranes have been taken in different liquid solvents for two days at 20 °C. After taking out, the excess liquid has been removed by filter paper and the weight of the membranes has been determined.

Figure 11 demonstrates the decrease of the solvent uptake U of our membranes with the molar volume V_m; only for T900 is $U(H_2O) < U(CH_3OH)$. In the case of this polymer with a low content of OH groups a larger affinity of the CH_3 groups of methanol to CH groups of the membrane may play a definite role. For all solvents, $U(E320) > U(K700) > U(T900)$ is valid. May be the large OH affinity to the membrane material plays an important role. This is shown by the solubility of unpolar solvents in our membranes (Table 3).

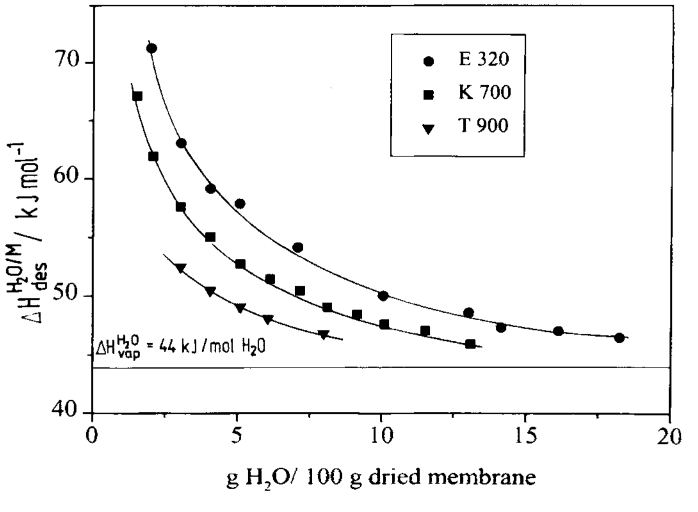


Fig. 10 The desorption enthalpy, ΔH_{des}, for the different membranes for different amounts of adsorbed water

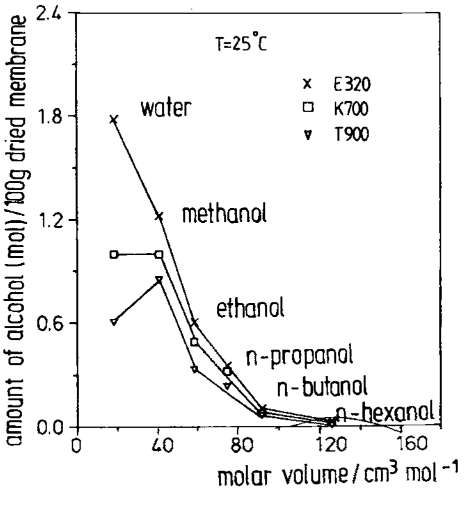


Fig. 11 The sorption of different alcohols and water by the three membranes as a function of the molar volume at 20 °C

Table 3 Uptake of unpolar solvents at 20 °C/(mole solvent/100 g membrane)

Solvent	E320	K700	T900	V_m [ccm mole^{-1}]
CCl_4	0.0083	0.0047	0.0039	96.5
n-Pentane	0.0164	0.0119	0.0099	115.2
n-Hexane	0.0148	0.0118	0.007	130.5
n-Octane	0.0099	0.0077	0.0048	162.6
Cyclohexane	0.0115	0.0071	0.0042	108.1

The taking up also shows the tendency to decrease with the size of the solvent molecules in the case of the CH_2 containing molecules. Only CCl_4 plays a different role. This could be explained by the sphere-like geometry compared with the more chain-like geometry of the paraffins. The membrane series of the solvent uptake is similar to the series of the water uptake. The amount of nonpolar molecules' uptake (in moles/g) is much smaller (less than a factor 1/100) than for the alcohols (Fig. 11) and for water (Figs. 2–4).

The uptake of solvents by membranes dried at 110 °C in moles/100 g membrane is similar to the rest of water in the membranes which are only dried in the presence of P_4O_{10} at $p/p_0 = 0$ at 20 °C (see Figs. 2–4).

Discussion

These reported experiments suggest the hypohtesis that the unpolar solvents are absorbed by small holes inside the membranes or at its surfaces. Such holes could have a statistics of sizes, and larger molecules could only invade relatively larger holes with high affinity. The remaining water molecules after drying with P_4O_{10} could also be adsorbed in such holes.

Besides water adsorbed in holes, water and alcohol molecules within the membrane swell the membrane by their affinity to the OH groups of the matrix. During a swelling process energy to separate the cellulose acetate groups is needed; energy for "hole production" is required. This is not necessary for holes, which exist already before contacting solvents, or the "rest" water (Table 4) has a larger adsorption heat and is therefore not desorbed by P_4O_{10}.

Our observations indicate three (or more) different adsorption mechanisms of water and alcohols:

1. A small amount in holes with a certain distribution of sizes. The product of adsorbed amount moles times the molar volume V_m gives an estimation of about 0.5–2 cm^3 holes per 100 g membrane. This small amount can be neglected in swollen membranes.
2. A first layer of a hydrate or an alcoholate.
3. Further water has a more or less liquid like structure. The cooperativity of the H-bonds [14] induces stronger H-bonds in layers farther away from the membrane groups and favors increasing swelling processes.

Table 4 Remaining H_2O Rest after drying the membrane over P_4O_{10} at 20 °C (cf. Figs. 2–4)

	E320	K700	T900	V_m [ccm]
mole H_2O/100 g membrane	0.065	0.04	0.016	18

In this way the affinity of water at larger p/p_0 increases with the water amount (see Figs. 7 and 8). Thus, the cooperativity effect causes the swell of the media.

BET adsorption

The adsorption could be described for $p/p_0 < 0.3$ in an approximation as a two energy mechanism (Figs. 7, 8 and in [6]). A two energy mechanism is assumed by the so-called BET adsorption isotherm (Brunauer–Emmet–Teller [15, 16]). We found such BET isotherms from $p/p_0 = 0$ to $p/p_0 = 0.3$ or 0.4, respectively [6].

The BET theory assumes two adsorption energies for the multilayers: 1. ΔH_{des} of the hydrate layer and 2. $\Delta H_{vap}(H_2O)$ for all higher water layers. – This assumption is very approximate from the point of view of our spectroscopic cooperativity mechanism. We have to expect that water layers 2–4 have different H-bond energies. More than 4 layers seem not to exist if we compare the amount of water adsorbed as hydrate and in higher layers. This amount could be estimated spectroscopically. The results will be published in a future paper [17]. Table 5 gives values of ΔH_1 in kJ mol^{-1} and W_m in g H_2O/100 g dried membrane if we apply the BET equation to our experiments up to $p/p_0 = 0.3$.

W_m in Table 5 gives the amount of water which fills the hydrate layer. In the next line are given the experimental p/p_0 values at which W_m exists in the membranes. The last line gives the corresponding energies: $\Delta H_1 = \Delta H_{des} - \Delta H_{vap}(H_2O)$ for the W_m of Fig. 10. The agreement between the BET values and our experimental ones is fairly good and demonstrates that, up to $p/p_0 = 0.3$, a two energy mechanism is a useful approximation. Alternatively, we have to conclude that the water adsorption at larger p/p_0 is a multilayer mechanism. This mechanism

Table 5 Constants derived from the BET equation

	E320	K700	T900
ΔH_1 [kJ mole^{-1}]	13 + 2	10 + 2	6 + 2
W_m [g(H_2O)/100 g (membrane)]	4.9	3.8	2.8
p/p_0 (W_m)	0.22	0.26	0.33
ΔH_1 [kJ mole^{-1}(W_m)] (Fig. 10)	14	12	9.9

Table 6 Densities in g cm^{-3} at 20 °C

Diethylether	0.714	Sucrose	1.58
Ethylacetate	0.901	Sucrose-octylacetate	1.27
Methylacetate	0.934	Cellulose	1.27–1.6
Fructose	1.6	Cellulose-acetate [20]	1.3
Xylose	1.52		

is expected by our knowledge of the cooperative H-bonds in liquid water and will be established in a future paper [17].

The W_m-values of the BET equation in Table 5 agree approximately in Figs. 7 and 8 with the water amounts at the end of the linear decrease of the partition coefficients in the region of small p/p_0.

The failure of the BET equation with the assumption of two adsorption heats in the region for $p/p_0 > 0.4$ (Table 5) indicates the existence of more than two adsorption heats in the region of the increase of the water partition coefficients (see Figs. 7 and 8 at large p/p_0). This could be related to an increase of the H-bond cooperativity between a number of water H-bonds. The H-bond interaction increases with the degree of cooperativity. On the other hand, the van der Waals interaction energies are smaller in the region of water multilayers because the structure of liquid water with low coordination numbers near 4 appears more and more.

In a spectroscopy paper [17, 6] we established our previous result [3] that the H-bond energies between the hydrate water in the membranes are smaller than $\Delta H_{vap}(H_2O)$ and correspond to H-bonds between water and ether or acetate. The observation in this paper and in [5]: $\Delta H_{des} > \Delta H_{vap}(H_2O)$ in contrary to the spectroscopic result may be caused by the van der Waals interaction energy between the hydrated water and the membrane groups to be larger than in liquid water. Probably, the coordination number [18] of the hydrate water in the membrane is larger than 4 as in liquid water.

In approximation, the van der Walls interaction is correlated with the density of similar compounds. One example of this tendency has been observed by the solvent effect on the IR frequency of monomeric methanol molecules by n-paraffins with different chain length [19]. This hypothesis of larger van der Waals forces acting in the membrane hydrates becomes more probable if we compare the densities of simple ethers or acetates with the values of cellulose acetate or cellulose (Table 6).

The so-called Badger–Bauer rule, the correlation between the IR frequencies and the H-bond energy [21, 22], also exists between the IR frequencies and the van der Waals energies [23, 24]. However, van der Waals interaction energies shift the OH vibration frequencies much less than those of H-bonds. This explains the relatively small IR shifts of water hydrates in cellulose acetate and the apparant discrepancies between IR results and measured adsorption energies. The IR method also give a quantitative estimation of three adsorbed water species: (1) hydrate water, (2) liquid like water and (3), a rest of water a structure between the hydrate and liquid water [17].

Acknowledgement We thank Dr. Wolfgang Pusch for the preparation of the membranes and for good cooperation. We are grieved that Dr. Pusch has fallen a prey to a criminal and could not continue his excellent work on sea-water desalination membranes. We thank Dr. Hubertus Kleeberg and Fa. Trifolio Lahnau for discussions.

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