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INVESTIGATION OF THE WETTING BEHAVIOUR OF NATURAL LIGNIN - A CONTRIBUTION TO THE COHESION THEORY OF WATER TRANSPORT IN PLANTS

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SUMMARY

Measurements of contact angle, contact heat and water vapour adsorption properties of milled wood-lignins and lignins from the Organocell process permit the conclusion that the natural lignin of the vessel walls in the xylem of plants is unwettable. Microscopical investigations of wood samples of several species of trees showed an apparently well-planned pattern of distribution of lignin over the water-contacted surface of the vessel wall. Strongly lignified unwettable domains are surrounded by very wettable cellulose. The pits of the vessel walls are considered as an example for this distribution pattern. Investigations by a water immersion microtechnique with fresh plant material could prove that gas accumulates in the pit hollows.

The existence of a large number of unwettable domains on the vessel walls which cause gas accumulation is incompatible with the cohesion theory of water transport. An explanation for the water transport is given alternatively to the cohesion theory which implicates wall-adherent gas bubbles and is based on positive pressure. The vessel walls covered by a large number of adherent microbubbles present a thermodynamic system in a state of metastability. The evaporation of water by transpiration deflects this system far from its relative minimum of free energy. In this energy charged condition the system is able to take up water from the soil and swings back to its energetic minimum. For an external observer the water conducting system of the plant seems to be under negative pressure. Physiological phenomena such as guttation, xylem-exudation and stem shrinkage as well as the experimental pressure bomb readings are consistent with this model of water transport.

INTRODUCTION

Water transport through the xylem of higher plants is, according to the cohesion theory (ref. 1), a flow under negative pressure. In accordance with this theory the high cohesive strength of water and its strong adhesion to the walls of the tracheary elements guarantee the continuity of sap flow from the root to the leaf.

Although the adhesion of the water to the vessel walls is part of the basic concept of the cohesion theory, this adhesion has not until now been closely investigated. One presumes that cellulose

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as the main hydrophilic component of the vessel walls causes a strong adhesion of water to the walls. The lignin however, as a structural component of the cell walls and just as important as cellulose, is almost never considered. Reference to lignin in relation to the water transport is found in W.F.Pickard (ref. 2), who having referred to an investigation by S.B.Lee and P.Luner (ref. 3) assumed that the behaviour of the lignin of the vessel walls is a hydrophilic one. This assumption has to be questioned however because it is based on wetting measurements taken from denatured lignins from the paper industry. Normally the lignin of the cell walls is considered as poorly hydrophilic (ref. 4). Recent investigations into the lignification process even came to the conclusion that it has to be considered pronounced hydrophobic (ref.5).

The aim of the following investigation was first to get a better wettability assessement of the lignin of the vessel walls. To do this the wetting properties of lignin (that is lignin extracted as near to its natural state as possible) were measured. Based on these results we then tried to show a correlation, that went beyond the classic cohesion theory, between the movement of water through the xylem and the adhesion of water on the heterogeneous cellulose/lignin composite of the vessel walls.

EXPERIMENTAL

The experimental investigations are sectioned into wetting measurements of extracted lignins and into microscopical examinations of plant material. Additionally some experiments with model systems were carried out.

Physicochemical investigations

(1) Materials. Lignin cannot be extracted from the raw plant material unaltered. In order to remove lignin macromolecules from the cell wall they have to be broken down. This is done preferrably by cleavage of the ether linkages which leads to an increase of the phenolic OH-groups. The proportion to these and other hydrophilic groups is therefore higher in extracted lignins than in the natural polymer lignin. The wetting characteristics of extracted lignins would thus also show stronger hydrophilic properties than a measurement taken from the unobtainable natural lignin of the cell wall.

The lignins to be measured (see Table 1) were specifically selected with respect to their similarity to natural lignins. They were extracted according to either the Björkman process or to the Organocell process (ref. 6-7).

The Björkman-lignins (milled wood-lignins) are of relatively low molecular weight, however they are, to a large extent, chemically unaltered.

In the Organocell process the delignification is effected by a two stage pressure cooking with methanol/water solutions under the addition of sodium hydroxyde in the second stage. The lignin extracted in the first stage is similar to the milled wood-lignins but due to just its technical purity it has a higher content of hydrophilic polyoses, that influence the wettability, than the milled wood-lignins carefully purified in the laboratory.

The lignin from the second stage was precipitated from an alkaline solution by phosphoric acid. It has a higher molecular weight but has to be seen as being more denatured.

TABLE 1
Investigated materials

Material	Designation	Species	Classification	Source
Björk-mann-lignins	MWL1	Metasequoia glyptostroboides	Gymnospermae	BFA Hamburg
	MWL2	Betula pendula	Angiospermae	
Organocell-lignins	TL1	Picea abies	Gymnospermae	Organo-cell München
	TL2	Picea abies	Gymnospermae	
native cellulose	C1	unknown		Merck Darmstadt

Concerning the similarity to the natural state one can classify our lignins in the order: TL2 - TL1 - MWL1/MWL2(best similarity).

With the aim of a qualitative comparison IR-spectroscopy was carried out from all the investigated lignins (see Fig. 1). More details about the elementary analysis, the functional groups and the molecular weight distribution of lignins from the Organocell process in comparison to milled wood-lignins are given by A.Lindner und F.Wegener (ref. 7).

For comparative purposes a purified native cellulose of commercial quality was included in the investigation. (As the

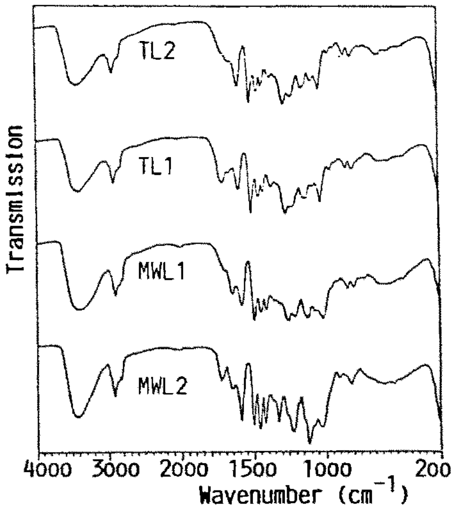

Fig.1. IR spectra of the investigated lignins.

Differences in the carboxyl and the carbonyl groups were indicated at 1710 and 1670 1/cm. Further the gynosperm lignins differ from the angiosperm lignin in the range 1200 to 1400 1/cm due to their different monomers.

cellulose in contrast to lignin constitutes to a large degree a chemically uniform natural product the lack of detail about the botanical source is not of significance.)

(2) Contact angle. The contact angle is the most important wetting characteristic. As lignins, however, can only be obtained in powder form it is difficult to carry out measurements of the contact angle. To get the necessary plane surface for measuring, the lignin has either to be plastified and compressed into test samples or it has to be transferred from a solution into a smooth film on to an even glass plate.

It is not advisable to use the compressed sample method because the high temperature needed for plastification would lead to a chemical change of the lignins. The preparation of a lignin on a glass plate was successful only with TL1, which is completely soluble in methanol. All the other lignins were only partly soluble in different solvents. Therefore the measurements of the contact angle on such films would have shown unreliable results.

The contact angle measurements on the lignin TL1 was carried out accordingly to the sessile drop method in a climatised chamber. In accordance with Lee and Luner we found a decrease of the contact angle depending on the contact time (see Fig. 2). However a reduction of the contact angle to zero degrees was not ascertained - even after several hours of contact. The advancing contact angle remained stable at 63° after the lignin had been saturated by absorbing water.

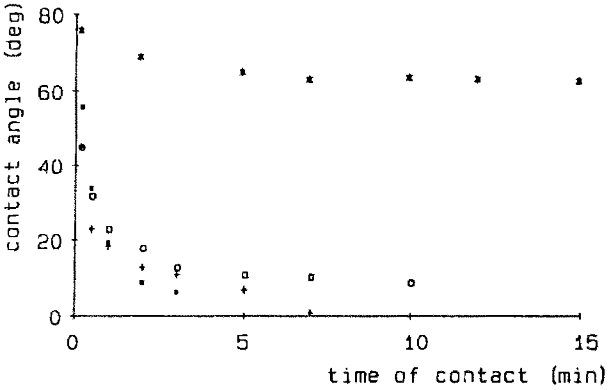

Fig. 2. Advancing contact angle of lignin/water
(*) lignin TL1 at relative air humidity RH 96%
(+),(o),(▫) technical lignins ref. 3 at RH 84%.

Because the contact angle measurements had been limited to lignin TL1 other methods had to be found out in which we were able to take measurements on powdery substances too. Using the contact angle of TL1 as a reference value it was possible to assess the wettability of the remaining lignins.

(2) <u>Contact heat</u>. The heat which resulted from stirring vacuum dried lignin*p.41 into water was measured in a calorimeter**p.41 .

Upon immersion of the powder in a liquid, the original solid-gaseous surface is transformed into a solid-liquid interface of the same size. The system "interface" thereby exchanges reversibly isothermal and isobar work and heat:

$$dU = A\, d(\Delta\sigma) - T\, A\, d(\Delta\sigma)_{p,A} \qquad \text{with} \quad \Delta\sigma = \sigma_{sl} - \sigma_{sg}$$

s solid; l liquid; g gaseous; U inner energy (J); A area $[m^2]$;
T temperature[K]; p pressure $[N/m^2]$; σ interfacial tension [N/m]

When immersing, the released work is converted to heat inside the calorimeter and can be measured together with the immersion heat. If, by immersion hydration occurs, a hydration heat is generated too and will be measured additionally. The sum of the three terms of heat will now be termed contact heat.

The contact heat of various powdery substances can only be compared with each other when the respective powder surface is known. The surface measurement was carried out by the nitrogen adsorption method according to Brunauer, Emmett and Teller (BET-method) in the simplified form described in DIN 66132 as the one-point method of Haul and Dümgben (see Table 2).

TABLE 2
Calorimetric measurements

Material	Calorimeter (J/g)	BET-value (m^2/g)	Contact heat (J/m^2)
TL1	15,29	4,35	3,51
TL2	50,998	4,54	11,23
MWL1	41,558	33,65	1,24
MWL2	54,40	29,94	1,82
C1	47,388	3,20	14,81

Concerning the thermal coefficient of the surface tension, the following is true:

$$d\Delta\sigma/dT = d\sigma_{sf}/dT - d\sigma_{sg}/dT \qquad \text{or approx.} \qquad d\Delta\sigma/dT = d\sigma_{fg}/dT$$

For water at 293,15 K is d $\sigma_{fg}/dT = 1{,}46\ 10^{-5}$ J/m·Kelvin. This value is virtually the same for all substances that are completely wetted by water (ref. 8). Because of measuring this term of heat together with the above mentioned immersion heat - both of approximately the same quantity - a value of about 0,1 J/m^2 had to be expected in the calorimeter in case of complete wettability. As it is shown in Fig. 3 however the heats related to the BET-surface are significantly higher and range from 1,5 to 12 J/m^2. Therefore it is evident that the measured contact heats of our lignins show substancial heat of hydration. This was made still clearer by comparing measurements with a native cellulose capable of hydration, which shows a value of 14,85 J/m^2.

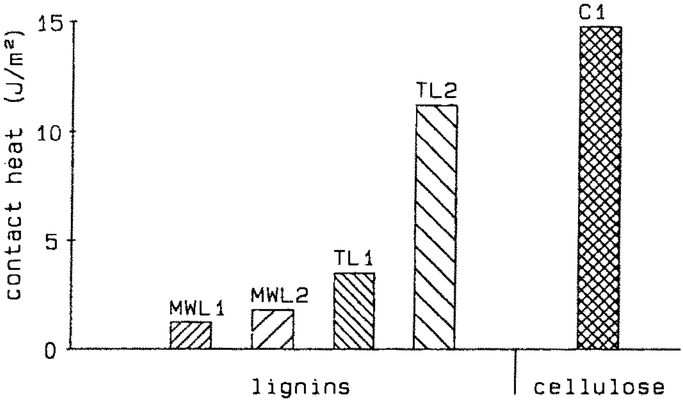

Fig. 3. Contact heat of lignin/water and cellulose/water related to the BET-surface.

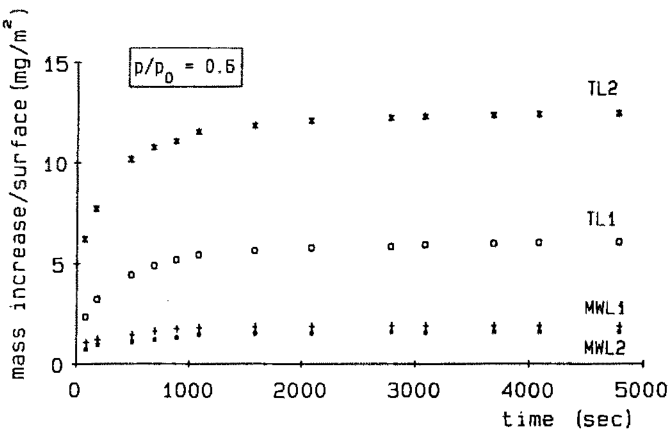

Fig. 4. Velocity of water vapour adsorption by lignins
p partial pressure of water in the air.
p_o saturation pressure of water vapour.

The hydration does not only take place on the surface, but penetrates the matrix by diffusion process. Thereby a further uncertainty is attached to the results of our calorimeter readings.

Although the immersion heat of the investigated lignins could not actually be recorded, the obtained results are informative in order to assess the wetting behaviour: it clearly shows a tendency of a decrease in the contact heat corresponding to the approximation to the natural state of lignin.

(3) Adsorption of water vapour. The adsorption of water vapour (physisorption) is achieved as well as the wetting by v.d.Waals-forces. Thus no adsorption of water can take place, when the material is not wettable.

The adsorption measurements were carried out in a climatised chamber at a constant temperature of 20°C and different partial pressures of water vapour. The weight increase of the vacuum dried lignin samples were continuously registered to a degree of 0,01 mg.

The diagram "Adsorption velocity" (see Fig. 4) shows that the water saturation of the milled wood-Lignins MWL1 and MWL2 is already reached after 1000 sec. In comparison to that the Organocell lignins TL1 and TL2 show a slow weight increase even after 5000 sec. This indicates that one can assume that there is a swelling process due to hydration by the latter.

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* A turbomolecular pump was used to generate a vacuum of $5 \cdot 10^{-4}$ mbar free of hydrocarbons.

** Calorimeter LKB 8721-1 from LKB Producter, Bromma, Sweden.

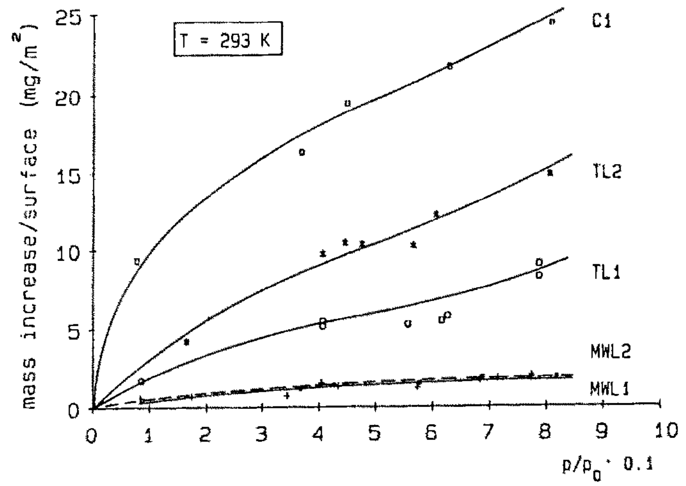

Fig. 5. Isotherms of water vapour adsorption by lignins
p partial saturation of water in the air.
p_o saturation pressure of water.

The diagram "Adsorption isotherm" (see Fig. 5) shows a very steady course with a definite saturation point for the milled wood-lignins. The isotherms of the Organocell lignins are of a completely different type similar to that of cellulose. It is known that this typeof isotherm indicates stronger interaction between the liquid and the solid phase than that is effected by v.d.Waals-forces.

Usually no monomolecular adsorption layers are formed by the physisorption, but an irregular multimolecular covering developes. On quartz as an example for the complete wettability, a water layer of 4 to 5 nm thickness will be formed on a flat smooth surface (ref. 9). With powdery substances it can be assumed that in case of complete wettability due to capillarity condensation even additional water is retained.

The saturation value of 1,8 mg/m^2 for the milled wood-lignins MWL1 and MWL2 can be converted into a layer thickness of adsorbed water of 1,8 nm. Compared to the 4 to 5 nm on a completely wetted flat surface it can be concluded that the investigated milled wood-lignin powders are incompletely wettable.

On the other hand the calorimetric measurements have shown that heat is released when the milled wood-lignins come into contact with water. This heat is much higher than the theoretical maximal possible heat a complete wettable substance could ever release.

That leads to the conclusion that milled wood-lignins essentially take up the water by chemisorption and hardly at all by physisorption. It seems that after having been taken up the chemisorption water to the inner no additional physisorption water will adhere to the surface.

All the applied measuring methods showed a uniform tendency to a decrease in hydrophility corresponding with the increase in the similarity to the natural state of the lignins. With reference to the contact angle of 63^{o} for lignin TL1 and in conjunction with the adsorption results from all the measured lignins one can extrapolate for the higher polymeric natural lignin of the vessel walls a contact angle of about 90^{o} and that is practically unwettable.

The lignin distribution in the surface of the vessel walls

If unwettable lignin in the surface of the vessel walls is in contact with water then there is no prerequisite for the even high wall adhesion which is what is claimed in the cohesion theory. However when considering what is known about the distribution of lignin in the surface of the vessel walls, it appears that nature does not intend to have complete and uniform wettability. In fact it seems that there is a pronounced tendency towards a complicated pattern of a non-uniform wettability.

Generally known is, that there is a stronger lignification in the spiral and reticulate thickenings of the vessel walls (commonly in herbaceous plants) compared to the rest of the vessel wall (ref. 10). In the consensus of the cohesion theory the thickenings are considered as mechanical supporting elements which stabilize the vessel walls against the negative pressure of the transported water. On the other hand the thickenings as they are strongly lignified represent, from our viewpoint, parts of the vessel wall where there is a reduced adhesion of water. Undoubtedly the latter would detract the tensile strength of the water column in the vessel tube.

A further example of non-uniform wettability of the water contacted walls is the wart structure in conifer tracheids (ref.11). The wart structure whose chemical composition is not fully known and whose physiological function is completely unknown gives staining reactions for lignin. (In addition to lignin, accrustations of other yet unknown polyphenolic compounds also give staining reactions by phloroglucin-HCl (ref. 12). Their wettability should be investigated.)

A typical feature of the vessels and tracheids are the pits. A pit is a region of the cell wall where no thickening is laid down on the primary cell wall. The function of the pits is assumed to guarantee radial water transport from vessel to vessel and to prevent expansion of gas volumes generated by embolism and cavitation. Between this physiological function and the chemical nature of the pits no conjunction has been seen until now.

In a short examination we found that by microscopical observation even of unstained samples of wood under suitable lightning conditions colour differences and differences in reflectivity are visible in the pit hollows. By the phloroglucin-HCL-staining reaction a corresponding inhomogeneous distribution of red-stained lignin will be seen as demonstrated in Fig. 6 for Vitis vinifera and Quercus robur. For better explanation of these findings we have marked the stained areas into scanning electron micrographs (which themselves do not indicate material differences).

The author realizes that further proof is needed to show that the pits are characterized by a extraordinary lignification. However this not yet sufficiently substantiated hypothesis is essentially supported by the following investigation of the actual wetting state of the vessel walls in living plants.

Actual wetting state of the vessel walls

Water from soil taken up by the plant is not free from dissolved gases. As the water rises in the plant its temperature increases with a concomitant tendency of degassing of the water.

Under these conditions the formation of a gas nucleus leads to a sudden vaporisation of the water being under negative pressure. By this local interruption of the water column the transpiration flow in the concerned vessel will be stopped. Because a large number of such events has to be expected, it would be expected that the water transport in the whole plant will be stopped after a certain time. But in reality this does not occur. Therefore in plant physiology it is assumed that plants provide a still undiscovered mechanism which spontaneously corrects the interruptions of the water column (ref. 13). However no real concept has been found to the physico-chemical nature of this hypothetical mechanism. Thus embolism and cavitation have to be considered the weak points of the cohesion theory.

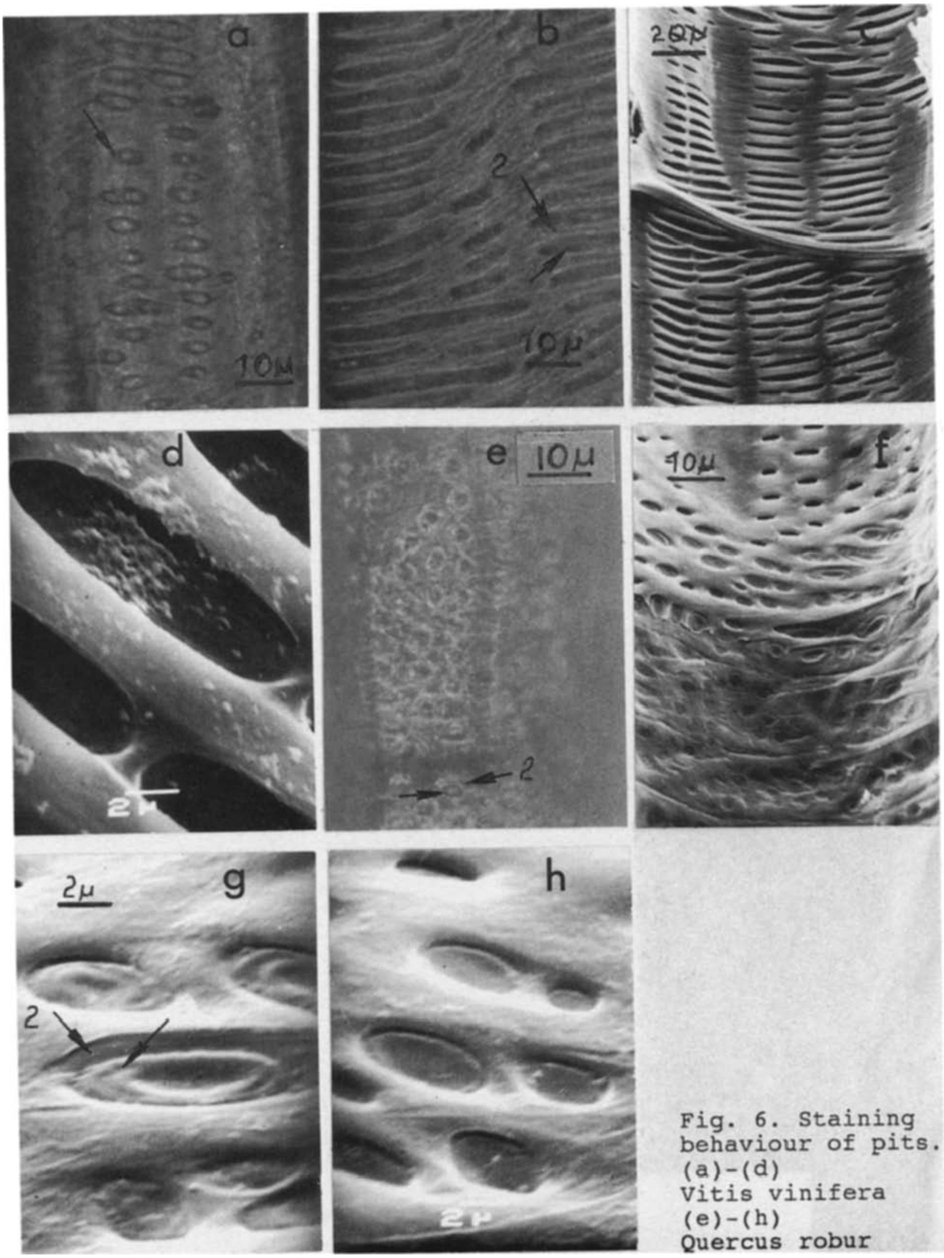

Fig. 6. Staining behaviour of pits.
(a)-(d)
Vitis vinifera
(e)-(h)
Quercus robur

The optical micrographs (a), (b) and (e) are showing red-stained (here dark) areas in the pit hollows (see arrows). In the pit hollows a stained ring shaped zone is bounded by an unstained surrounding and by an unstained center. Several pits are showing two concentric stainable rings (see arrow 2). The SEM-micrographs (c),(d),(f),(g),(h) are showing the pits in a higher magnification. The stainable zones are marked by arrows.

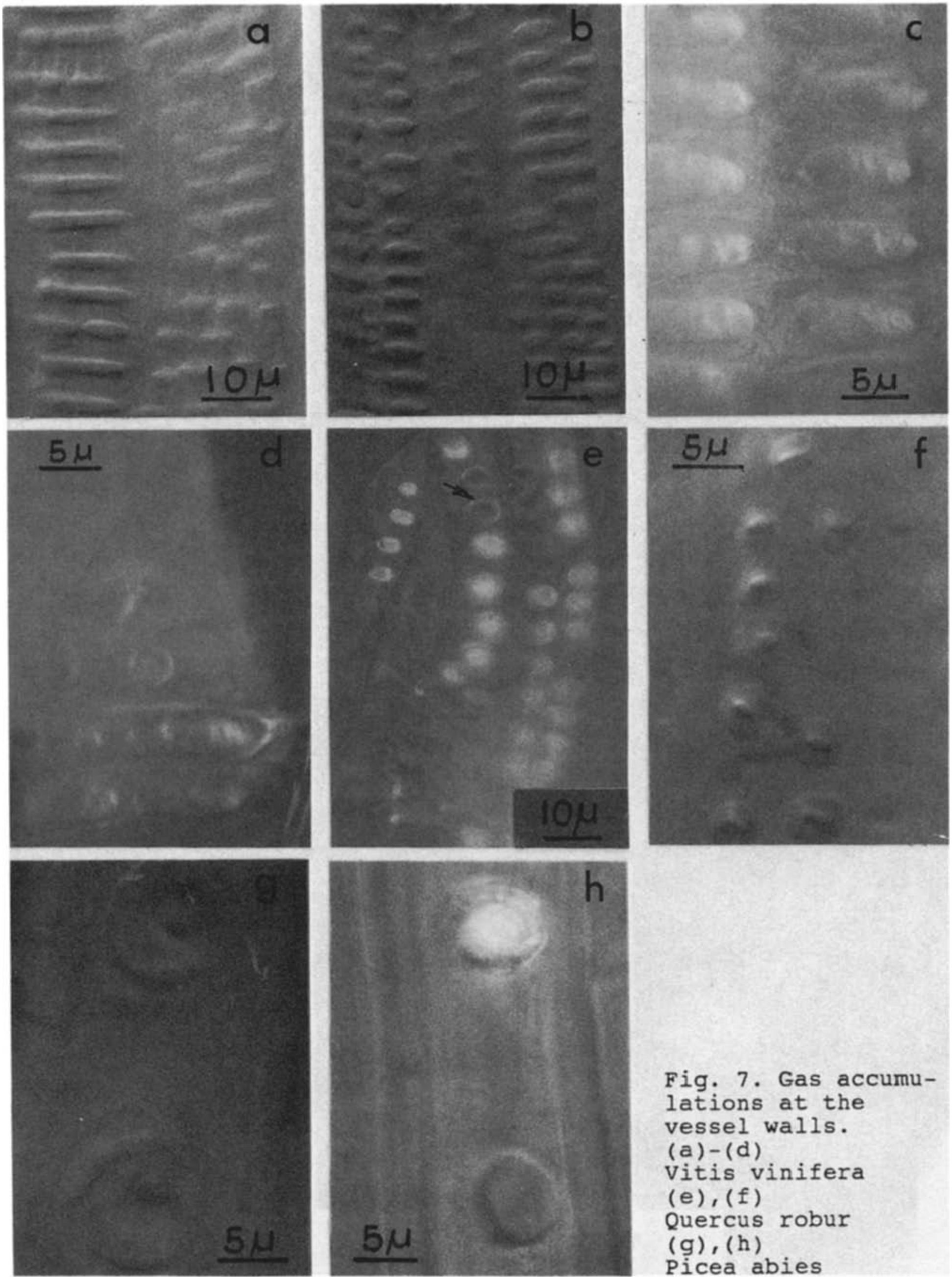

Fig. 7. Gas accumulations at the vessel walls.
(a)-(d)
Vitis vinifera
(e),(f)
Quercus robur
(g),(h)
Picea abies

(e) is showing that gas accumulates at the phloroglucin-stainable ring shaped part of the pits (see arrow). The neighbouring totally reflecting circle shaped areas not necessarily represent hemispherical bubbles. Probably they are double-walled shapes similar to Fig. 10 (d). (h) is showing the gas accumulation at two bordered pits where the upper one is in total reflection.

If there is a location of unwettable lignin on the surface of the vessel walls this has to be a centre of gas accumulation, because it is here that the smallest amount of energy for the formation of a gas nucleus is needed. Indeed, this we could prove.

Before break to leaf (end of april) three year old branches from different tree species were bent down into a container of iced water and samples of approximately 3 cm length were cut off. On these samples a tangential cut was made and then the sample, still immersed, transferred to under the microscope which was equipped with a lens* for water immersion. The whole procedure lasted only a few minutes.

All examined samples showed accumulation of gas in the pit hollows. These gas accumulations were visible under certain lighting conditions by total reflection at their gas/water interface. Fig. 7 is showing the gas accumulations at the vessel walls of Quercus robur, Vitis vinifera and Picea abies.

For further evidence that the gas was accumulated ultrasonic impulses were directed toward the totally reflecting formations by using a small ultrasonic vibration device** directly under the microscope. The gas accumulations could then be moved and detached. An equivalent effect caused by adding of surfactants to the water. The gas detaching process was documated by video.

As can be seen on the micrographs the gas formations are not always bubble shaped, but in some pits total reflection is in the shape of a ring or a sickle. It was obvious that the gas had not yet covered all of the unwettable area. On other parts of the vessel wall where pits were very close together the gas bubbles united to form complicated shapes which also adhered to the vessel wall. Gas accumulation at the pits also could be found on Acer pseudoplatanus, Betula pendula, Ulmus glabra and Fraxinus excelsior.

Experiments with model systems

A feature of the pitting of the vessel walls is the rare occurrence of single pits. Either the whole vessel wall has pits or there are larger fields or chains of pits. When the pits effect an accumulation of gas at the vessel wall there must also be a special function of their closely packed grouping. The following experiments might give a hint to this (see Fig. 8-10).

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* Objektive "PLAPO" (160x/1,25 W), Leitz Wetzlar, Germany

** "Sonus 4" (18 kHz, 100 W), Littan Dental Products Europe

Fig. 8. Hydrophobic areas on a hydrophilic base. Immersing the model into air saturated water, gas accumulates on the hydrophobic parts of the surface. The gas accumulations are first lenticular, then half spherical bubbles.Further gas diffusion into the bubbles enlarge them causing a distortion. If one bubble comes into contact with its neighbour they unify into a larger, even stronger distorted bubble that clings to several unwettable plinths on the wall. Due to the deviation of shape of the bubbles from being spherical and resulting distortion of the bubbles the bubble bearing wall must be stressed by equivalent forces (see Fig. 9 and 10).

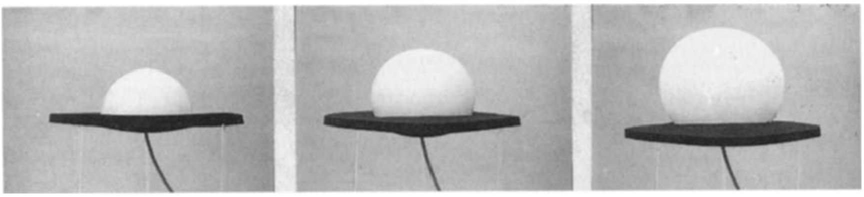

Fig. 9. A rubber balloon which is half spherical and inflatable is attached to an elastic rubber plate. (A taut rubber membrane has a similar behaviour as a liquid surface.) The line of contact of the mebrane to the plate cannot alter, just as a gas bubble that clings to a hydrophobic plinth. When overstreching the balloon by a high internal pressure results a distortion of the plate with a slope toward the pole of the balloon.

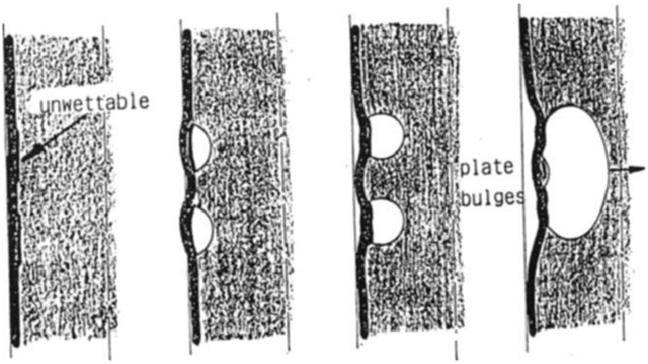

Fig. 10. When several bubbles unite - which cannot be demonstrated by balloon model - the whole plate bulges. Bubbles clinging to the inside of an elastic tube would cause the tube to contract.

DISCUSSION

The accumulation of gas which is found on the walls of the xylem vessels contradicts the existence of a negative pressure in the water conducting system. Also in contradiction to the negative pressure is the correlation between energy transport and energy dissipation in a flow due to a pulling force (that causes negative pressure).

In a pulled flow - unlike the flow under positive pressure - mass flow and energy flow would have opposing directions. The energy needed to accelerate a fluid particle into the flow first has to be transported from the exit of the flow (where the pulling force attacks) to its inlet. This conterflow of mass and energy in a deeper investigation would appear as a violation of the second law of thermodynamics and of momentum conservation.

On the other hand, however, a lot of physiological facts and not at least the well-known apparatus of E.Askenasy* (ref. 14) apparently indicate inevitably a negative pressure in the xylem. In the following a model of water transport will be developed that implicates the wall-adherent bubbles and that is based on a positive pressure. In this model the water column of the xylem externalizes as being under negative pressure.

An alternative model of water transport

Because of its high power demand the water transport through the xylem cannot be performed by the metabolic energy of the plant. The required energy obviously is transferred from the outside to the plant. Because the water transport is conjungated with the water lost by transpiration the energy transformation (at least to potential energy of the lifted water) should occur directly at the place of transpiration, that is the leaf. In accordance with the cohesion theory the energy transformation takes place in the following way.

According to H.Ziegler (ref 15) the transpiration first effects a diminution of the water saturation of the cells adjacent to the gas phase. Thereby a shrinkage of these cells takes place and the capillaries of the cell walls become narrowed. When the trans-

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* This experiment is cited in plant physiology as a convincing physical proof of the soundness of the cohesion theory. But it has not until now yet been carried out under physically clearly determinated conditions. Therefore - not without justification - it is occasionally remarked (ref. 16) that the conclusions from this experiment are possibly a false interpretation.

piration is continuing the menisci in the narrowed capillaries will shrink back and thereby become distorted. In this condition the menisci are considered as being able to pull up the water from the xylem in a steady state flow.

The shrinkage of the transpiring cells and the thus caused dewetting of the capillaries of the cell walls represents a disturbance of the energy equilibrium existing in the non-transpiration state. The manner of propagation of such a disturbance into the conducting system of the xylem and finally down to the place of water uptake (the root) depends on the wetting behaviour of the vessel walls. If the vessel is completely wetted then the vessel tube represents an energetically neutral pipeline.No energy transformation occurs when the hydrostatic pressure of the water alters If the water column is higher then 10m the power transmission from the leaf to the root is imaginable only by pulling forces but physically this cannot lead to a mass flow as explained above.

If gas bubbles adhere to the vessel wall the bubbles have to react to a variation of the hydrostatic pressure in the water column. If the vessel wall has elastic properties it becomes distorted by the bubble forces. The wall distortion is in interaction with the hydrostatic pressure too. With certain simplifications for the energy the following is true:

$$dE = Fds + \Sigma\sigma_j dA_j + \Sigma\sigma_k dA_k - \Sigma p_j dV_j + \epsilon d\tau + vdP + \Sigma\mu_{i,j} dN_{i,j} + TdS$$

For a bubble free wall is true: $dE = Fds + \sigma_k dA_k + vdP + TdS$*

E total energy, s vertical translation, A surface, V gas volume, τ wall distortion, P momentum of translation, N moles, S entropy, F translation force, σ surface tension, p gas pressure, ϵ shearing modulus of the vessel wall material, v velocity, T temperature. i number of chemical components (gases and water), j number of bubbles adherent to the vessel wall, k number of microcapillaries in the mesophyll adjacent to the vessel tube (To accentuate the difference between the two systems, two terms of surface energy were introduced.)

For a completely wetted tube the evaporation from the microcapillaries leads to a dislocation of the menisci mentioned above. This meniscus dislocation results in an energy input by dewetting of the walls of the microcapillaries. However, the possible energy

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* With the assumption of a certain elastic wall distortion that could be effected by a strongly wall-adherent water column - when it is stressed - the term $\epsilon d\tau$ has to be added.

input into the water conducting system is fairly low because the totally dewettable capillary surface is very limited.

For a xylem tube, covered with a lot of wall-adherent bubbles, however, the transpiration leads to an energy charge of the whole tube wall.

The energy charging process starts with the deswelling of the mesophyll cells. The part of the tube that is embedded in these shrinking cells loses water as Ziegler described. The menisci of the microcapillaries pull water out of tube causing a drop of the hydrostatic pressure in this part of the tube. The pressure drop effects the growth of the bubbles which adhere to the wall. Consequently the diameter of the elastic tube will be constricted (see model system Fig. 9 and 10). The growth of the bubbles and the constriction of the tube leads to a further increase of the hydrostatic pressure and to a displacement of water as shown in Fig. 12. As a result of this a supply of water to the places of transpiration is effected. Secondly the equivalent mass of water (more exactly the equivalent momentum) is simultaneously pushed in the basal direction of the vessel tube. In this part of the tube the increase of the hydrostatic pressure leads to a bubble diminution. When no further water loss occurs in this stage the tube will be able to reduce its elevated free energy in the following way.

The energy equilibrium existing in a bubble bearing xylem tube has to be considered as a metastable one (see Fig. 11). No bubble is able to detach itself from the wall even when it is overstressed or several bubbles have united to form a larger complicated shaped bubble.

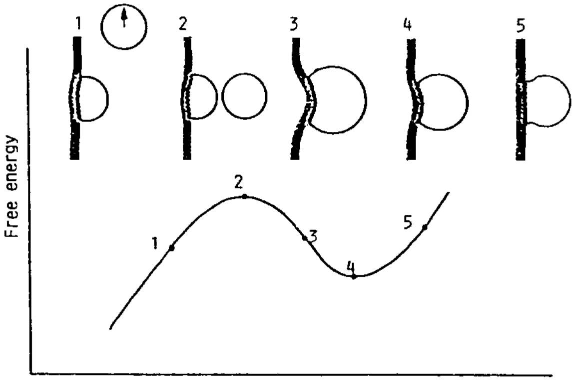

Fig. 11. Metastability of a single bubble, being in several stages of internal pressure.

Because the hydrostatic pressure (and to some extent the wall distortion) allows an energy exchange between the individual bubbles, two neighbouring bubbles are able to minimize their free energy. Finally the bubbles of the whole tube may minimize in the same way the total free energy of the whole tube.

When by transpiration a certain volume of water has been removed from the upper end of the tube the disturbance of the initial metastable equilibrium propagates with a limited velocity over the whole length of the tube.The process of bubble growing or shrinking is, as each surface alteration, conjugated with the exchange of heat with the surroundings and that takes time. The caused slowness of free-energy minimization in the xylem is of great importance. It enables an alternating energy charge and discharge of the vessel tubes. The discharge effects the antibasal movement of water in plants.

In the non-transpiration state a certain degree of water filling of a xylem tube is in accordance with the relative minimum of free energy. The water is sustained at the respective height because a decrease of the water column would cause a drop of the hydrostatic pressure and consequently the wall-adherent bubbles would expand. The bubble expansion, however, would require more surface energy and wall distortion energy then there is potential energy released by the decrease of height.

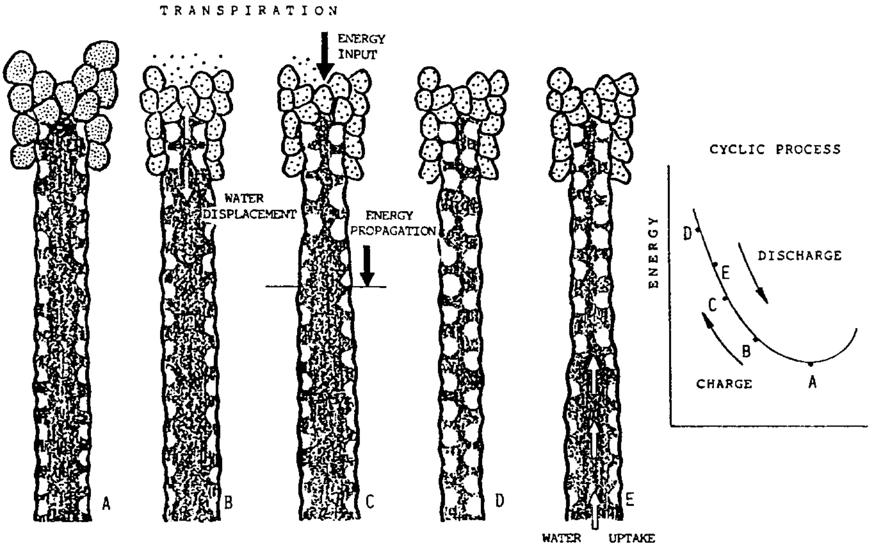

Fig. 12. Peristaltic energy charge and discharge of a xylem tube by alteration of the wall-adherent bubbles due to transpiration. The spherical shape of the bubbles is a graphical simplification.In reality each bubble is attached to the wall by several plinths (Fig.8)

When a water deficit occurs in the tube due to transpiration the system has a tendency to refill. The water intake into the vessels occurs where water is obtainable. This normally is from the root but also from the parenchym cells of the xylem or - as observed in certain cases - from the rain wetted surface of the leaves. The water is sucked into the vessels by the wall-adherent bubbles when they are shrinking and this simulates a negative pressure.

When comparing the water uptake by a system under negative pressure with that of a bubbles-on-the-wall-system, there is a significant difference in timing of energy input and effected water transport.

When the system is entirely under negative pressure then a further energy input at the menisci of the cell walls of the mesophyll should lead to an instant water uptake from the root. In accordance with the cohesion theory there is a synchronism of energy input and water uptake.

In a bubbles-on-the-wall-system, however, the water uptake is delayed. At first the water conducting tube system has to be charged with surface energy and wall distortion energy. Because of the slow energy propagation in the vessel tubes intially a considerable supercharging in the upper part of the tube takes place, depending on the intensity of transpiration. At this stage the water lost by transpiration is supplied only by water that is stored in the xylem. During transpiration the charged energy slowly propagates along the bubble covered walls of the vessel tubes. In this process the stomata are of significant importance as they control the transpiration. After stomata closure practically no more energy input occurs but the downward energy propagation continues. When this propagation of energy has reached the root water uptake from the soil begins.

In this model of water transport, the water movement does not represent a tubular flow in the precise sense of hydrodynamics. It is more apt to characterize it as an incessant rearrangement of the internal surface (this is very large considering the enormous number of wall-adherent bubbles) and the shape of the water catena of the plant in order to minimize the free energy of the system. In this mechanism the work of transpiration is primarily to disturb the metastable equilibrium of the system over and over again.

A model of water transport that implicates gases in the liquid and which considers a phase shift between transpiration lost and water uptake seems to be more consistent to physiological and experimental facts than a model based on negative pressure. This may be demonstrated by the following examples:

(1) Embolism. Gases in the transported water are not a perturbing factor in a bubbles-on-the-wall-model. The water transport works by utilizing the gas and is not hindered by it.

(2) Cavitation. Cavitation does not occur under positive pressure. Acoustic clicks (ref. 17) in wilting branches (as they are generally seen as evidence for the appearence of cavitation) can be explained by sudden surface rearrangements of certain groups of wall-adherent bubbles as could be observed under the microscope. But this point still has to be investigated.

(3) Pressure bomb readings. In its energy charged state the bubbles-on-the-wall-system is able to suck water. That looks from the outside like being under negative pressure. A displacement of the water column by an external positive pressure in the surroundings of the leaf (that is what is done by the pressure bomb) therefore can be claimed as a proof for a negative pressure or for a bubble system as well.

(4) Root pressure, xylem-exudation, ascent of sap in Spring. This group of phenomena represtens water transport without simultaneous transpiration. According to the cohesion theory no pulling force is acting. An active "vis a tergo" mechanism based on osmotic forces therefore is assumed but there is no real conception. In a bubbles-on-the-wall-model no metabolic forces are required. As has been proved microscopically the wall-adherent bubbles exist even in the central cylinder of the root. Therefore root pressure has not to be considered as an independent phenomenon of water transport.

Guttation occurs in our model, when the energy stored in the plant due to transpiration exceeds the energy level that is necessary for restoring the waterfilling is equivalent to the minimum of free energy (see Fig. 12). Xylem exudation and ascent of the sap in Spring might be explained by regeneration of the bubble formation on the vessel walls due to the increasing temperature in Spring. Details concerning reaccumulation of gas on the vessel walls cannot be given for the present.

(5) Shrinkage of stem diameter. This long-known phenomenon is explained in the cohesion theory by a stress transmission from the stressed water threads to the vessel tubes. This transmission is due to the strong adhesion of the water to the walls. In our

opinion it is the constriction of the vessel wall effected by expansion of the wall-adherent bubbles caused by a drop in the hydrostatic pressure.

(6) Radial flow. It is difficult to understand how radial flow can take place under tensile strength of the water threads. In our model of water transport radial flow is effected by relative differences in the deflection from the metastable equilibria in two neighbouring vessel tubes. If there is a passage from tube to tube the differences may be equalized by radial flow. In this way even overlapping cuts in the stem can be eliminated. As Greenidge (ref. 18) demonstrated the water moves round the cuts.

CONCLUDING REMARKS

The suggested model of water transport due to wall-adherent microbubbles is based on the antipodal wetting behaviour of lignin (maybe other unwettable compounds too) and cellulose and on a certain pattern of distribution of lignin and cellulose on the vessel wall surface. When there are microdomains of unwettable material are surrounded by wettable material the gas, dissolved in the uptaken water will accumulate on the unwettable domains. A wall-adherent gas bubble when it is expanding by further gas accumulation is unable to detach itself and comes into a metastable state of distortion . The entirity of the large number of bubbles, for instance adhered at the pits, represents a thermodynamical system that is able to be charged by a considerable amount of surface energy. By discharging its energy the system is able to lift water up to the place of transpiration the leaf. In this way the water transport of plants is effected in a hidden manner by surface forces as in many other biological processes

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